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Microstructure and Electrical Properties of PMN-PT Thin Films Prepared by Oxygen Plasma Assisted Pulsed Laser Deposition

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Abstract: Lead magnesium niobate-lead titanate (PMN-PT) ferroelectric thin films with composition near the morphotropic phase boundary (MPB) were deposited on Si substrate by oxygen plasma assisted pulsed laser deposition (PLD). Highly (001)-oriented PMN-PT thin films with lower oxygen defect and higher crystalline property were obtained. The results show that the microstructure and electrical properties of PMN-PT thin films strongly depend on the partial pressure and the activity of oxygen in the deposition process. With the use of oxygen plasma, the dielectric constant of the PMN-PT thin film is increased from 1484 to 3012, the remnant polarization ($2P_r$) changes from 18 μC/cm^2 to 38 μC/cm^2.

Key words: pulse laser deposition; PMN-PT thin films; microstructure; electrical properties

Relaxor-type $(1-x)PbMg_{1/3}Nb_{2/3}O_3$-$xPbTiO_3$ (PMN-PT) ferroelectric materials with composition near the morphotropic phase boundary (MPB) are considered as promising candidates for tunable devices, memory and MEMS applications due to their superior dielectric, ferroelectric and piezoelectric properties[1-3]. PMN-PT solid solution was consisted of relaxor ferroelectric PMN and normal ferroelectric PT. PMN-PT has superior electrical and piezoelectric properties when its composition approaches the morphotropic phase boundary (MPB). The composition of MPB for the PMN-PT binary system is usually considered as x=0.33−0.35. Over the past few years, PMN-PT thin films have been prepared by a variety of methods, including magnetron sputtering, Sol-Gel processing and pulsed laser deposition[4-7]. Among them, the pulsed laser deposition (PLD) has been proved to be an effective method for the growth of thin films with complex composition. However, the fabrication of high quality PMN-PT thin film with perovskite phase is still a challenge due to complicated influences of the oxygen partial pressure on the film microstructures and electrical properties. In the case of lower oxygen pressure, oxygen deficient PMN-PT films with pyrochlore phase could be easily produced, which gives rise to inferior dielectric and ferroelectric properties. Pure perovskite PMN-PT thin film could only be obtained under high oxygen pressure[6]. However, the increased scattering of ejected particles under high oxygen pressure would usually result in non-stoichiometric PMN-PT films. Besides, the oxygen pressure can also influence the morphology of thin film, and hence the leakage currents, dielectric and ferroelectric properties would be then affected. Therefore, the oxygen pressure would play a key role in governing the electrical properties of PMN-PT thin films prepared by PLD method. In present work, highly (001)-oriented PMN-PT thin films with low oxygen defect and high crystalline property were deposited on epitaxial $Ir/SrTiO_3/TiN/Si$ (001) substrate by oxygen plasma-assisted PLD, dependence of the microstructures and electrical properties of PMN-PT thin films on the oxygen pressure and its activity was investigated in detail.

1 Experimental

$0.67PbMg_{1/3}Nb_{2/3}O_3$-$0.33PbTiO_3$ (PMN-PT) thin films were deposited on Si(001) substrates by pulsed laser deposition system with the assistance of oxygen plasma. The stoichiometric PMN-PT ceramic mounting on a motor-driven rotary shaft was used as target. Si(001) substrates with epitaxial Ir(001) bottom electrodes were used to grow PMN-PT thin films. In order to avoid the lattice mismatch,

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$SrTiO_3$ thin film (100 nm) and TiN thin film (several nm) were used as intermediate layers between the Si substrate and Ir electrode thin film. The active substrates were therefore a hetero-structure of Ir/$SrTiO_3$/ TiN/Si (001). The deposition began when substrates were heated up to 650℃. A KrF(λ=248 nm) excimer laser system was operated at a frequency of 5 Hz, the laser energy density at the target surface was 5 J/cm^2. The oxygen pressure during the deposition was 2 Pa, much lower than earlier reported values[5, 8]. The oxygen plasma generator was placed between the substrate and the target. The working voltage and current of the generator were 0.4 kV and 40 mA, respectively. In order to examine the effects of the oxygen plasma, a control sample prepared without using oxygen plasma was deposited, during which, an optimum oxygen pressure of 27 Pa was adopted instead.

The crystallinity of the films was investigated by X-ray diffraction (XRD) (χ' Pert Pro MPD, Cu Kα, 0.154 nm). The morphologies were observed by field-emission scanning electron microscope (SEM) (JSM-6700F) and atomic force microscope (AFM) (SPI3800N). For the measurement of electrical properties, Pt top-electrodes with diameters of about 0.2 mm were deposited on the surface of PMN-PT thin films. The dielectric constants were measured by using a HP4294A impedance analyzer. The capacitance-voltage (C-V) properties were tested by using a Keithley 4200-SCS semiconductor parameter analyzer at room temperature. Ferroelectric properties were characterized by Precision Premier Ⅱ test system.

2 Results and discussion

The texture of substrates and lattice mismatch with PMN-PT thin films have significant influences on the quality of PMN-PT films[9-11]. Epitaxial Ir thin film with regular and compact grains is suitable for the growth of ferroelectric thin films[12-13]. Besides, the mismatch between perovskite phase PMN-PT (a=0.398 nm) and Ir (a=0.384 nm) is only 3.6%. Therefore, Ir electrode film grown on $SrTiO_3$/TiN-buffered Si(001) substrates was used as the bottom electrode. XRD patterns of the PMN-PT thin films on Ir/$SrTiO_3$/TiN/Si (001) substrate were shown in Fig. 1. Highly (00l)-oriented perovskite phase PMN-PT was obtained in thin films both with and without plasma, which indicated that epitaxial Ir(001) bottom electrode could induce PMN-PT stress-induced orientation effectively. The film with oxygen plasma exhibited better crystallinity due to the high activity oxygen density of oxygen plasma and the low deposition oxygen partial pressure. In the deposition process with 27 Pa oxygen partial pressure, the collision between the species evaporated from the target and the oxygen molecules is much more intensive than that in the low oxygen partial pressure, resulting in the poorer crystalline quality.

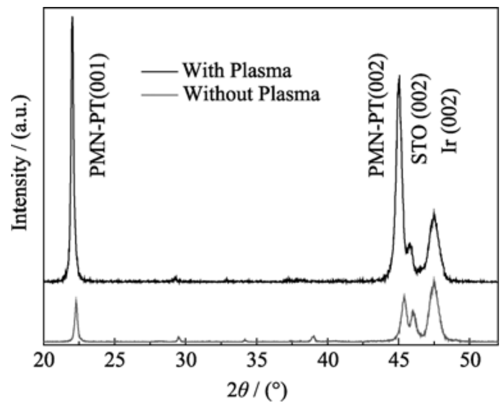

Fig. 1 XRD patterns of the PMN-PT films prepared with and without oxygen plasma assisted

The SEM images of PMN-PT thin films on the cross section were shown in Fig. 2(a) and (c), the thicknesses for both films with/without oxygen plasma are the same 360 nm. Compared with the loosely connected columnar structure in the film without oxygen plasma, the film prepared with oxygen plasma showed dense microstructure. Figure 2(d) showed the surface morphology of the PMN-PT thin films grown by oxygen plasma assisted PLD. The PMN-PT thin film exhibited a smooth surface morphology with a root-mean-square (RMS) roughness of 2.37 nm as recorded by a 1 μm×1 μm AFM scan. On the other hand, the grains formed under high oxygen pressure without oxygen plasma exhibited tapered dome shape and loosely-packed structure, as shown in Fig. 2(b). The film prepared without oxygen plasma exhibited much higher RMS roughness of 4.46 nm.

Dense thin film can effectively reduce the leakage current conducted through the grain boundaries. According to the current-voltage (I-V) test (as shown in Fig. 3), the leakage current of the film prepared with oxygen plasma, under an external electric field of 400 kV/cm, is about 10^{-7} A/cm^2 , much lower than that (about 5×10^{-5} A/cm^2) of the film prepared without oxygen plasma assisted. During the deposition process, the ions evaporated from the target surface would collide with oxygen molecules before reaching the substrate, which led to unfavorable energy losses. Moreover, the increase of oxygen pressure could also reduce the probability of atomic diffusion between the grains, and result in lower compactness and greater roughness. The increased activity of the oxygen density introduced by the oxygen plasma could effectively reduce the concentration of oxygen vacancy in low oxygen pressure conditions, and at the same time, avoid the negative effects of the high oxygen pressure during the deposition process.

The frequency dependence of the dielectric constant for PMN-PT thin films at room temperature was shown in

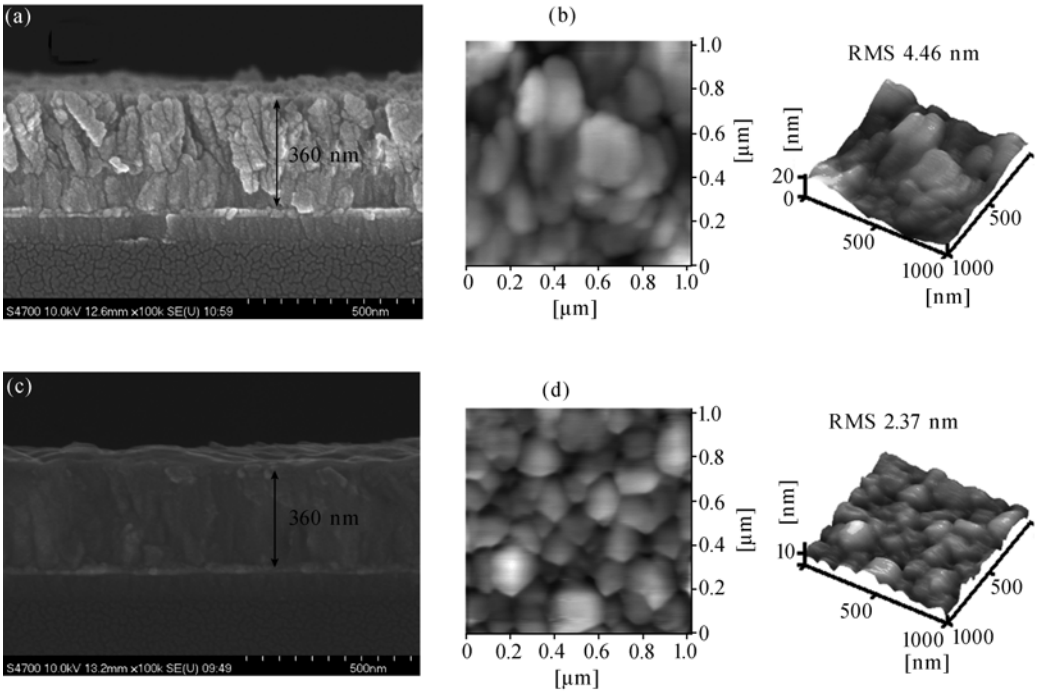

Fig. 2　Cross-sectional and surface morphologies of the PMN-PT thin films prepared (a) (b) without and (c) (d) with plasma assisted

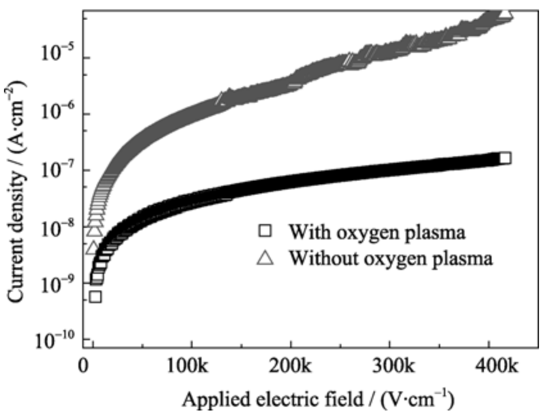

Fig. 3　*I-V* characteristics of the PMN-PT thin films

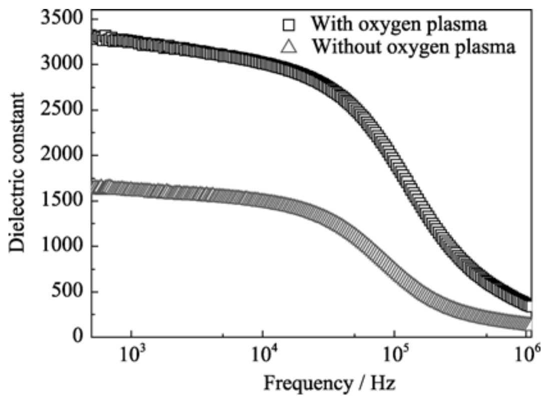

Fig. 4　Frequency dependence of the dielectric constant for the PMN-PT thin films

Fig. 4. The test frequency range is 500 Hz–1 MHz. The dielectric constants of PMN-PT thin films prepared with and without oxygen plasma at 10 kHz are 3012 and 1484, respectively. The dielectric constants were higher than the reported value in literature[14-15], which may be resulted from the pure perovskite structure and highly preferential orientation. The dielectric constant of PMN-PT thin films prepared without oxygen plasma assisted was lower than that of the film with oxygen plasma. The dielectric properties of ferroelectric thin films are closely related to the thin film microstructure and crystalline quality [4, 8, 15]. The PMN-PT film prepared with oxygen plasma had higher film density and better crystalline quality and thus possessed higher dielectric constant.

Figure 5(a) and (b) showed the polarization-electric field (*P-E*) loops for the PMN-PT thin films prepared without and with oxygen plasma under 414 kV/cm applied electric field. The PMN-PT thin film prepared with oxygen plasma showed good hysteresis property with a remnant polarization of $2P_r$=38 μC/cm^2 and a coercive field of $2E_c$=48 kV/cm. The shape of hysteresis loop of PMN-PT thin films is sloped and slim. PMN-PT is a typical relaxor ferroelectric material and has nanodomain structure[16-18]. The nanodomains of the relaxor can be oriented with the field leading to large polarization. However, most of these domains re-acquire their random orientation resulting in a small remnant polarization when the applied electric field is removed [19-20]. The PMN-PT thin film prepared without oxygen plasma exhibits a lower remnant polarization of

$2P_r$=18 μC/cm^2 and a larger coercive field of $2E_c$= 60 kV/cm. This poor ferroelectric properties may be related to the rough surface morphology and the defects formation during the deposition process (*e.g.*, oxygen vacancies), since the pinning effect of domain walls and defects of interface make domain switching in thin film much harder[21-22]. In addition, the *P-E* loop of the PMN-PT thin film prepared without oxygen plasma assisted exhibits stronger frequency dependence than the film prepared with oxygen plasma assisted.

Hysteresis circuits measure the switched charge *Q* instead of the polarization *P* directly. For a semiconductor ferroelectric film, the switched charge *Q* is given by[3]

$$Q = 2P_r A + \sigma E t \quad (1)$$

Where σ is the electrical conductivity, *E* is the applied electric filed, and *t* is the measuring time. The measuring time of 1 kHz and 10 kHz measuring frequency were 1 ms and 0.1 ms, respectively. As was mentioned above, the PMN-PT thin film prepared without oxygen plasma shows larger leakage current, thus the measuring frequency has larger influence on the switched charge *Q* according to Eq.(1). It can also be seen in Fig. 5(a) that, the *P-E* loops of the PMN-PT thin film prepared without oxygen plasma assisted shows a relatively flat shape, which can also be attributed to the effects of leakage currents.

Figure 5(c) showed the *P-E* loops of the PMN-PT thin film prepared with oxygen plasma under 5−15 V. It was observed that the hysteresis loops were a little asymmetry in shape. This asymmetry may result from the use of electrodes with different work functions and the different heat burden during the electrode depositions. The variety of remnant polarization and coercive field with applied voltage were presented in Fig. 5(d). It was found that the increment of coercive field was relatively small under higher applied voltage increase, indicating that the coercive field approached saturation.

The *C-V* curves of the PMN-PT thin films prepared without and with oxygen plasma assisted at a frequency of 100 kHz were shown in Fig. 6(a). The much obvious hysteresis loop of the PMN-PT thin films prepared with oxygen plasma assisted also indicated a better ferroelectric property. The PMN-PT is assumed to be as a p-type semiconductor due to the volatility of Pb. The “doping” density can be estimated from the *C-V* characteristics according to[23]

$$N_{\mathrm{dop}} = \frac{2}{q\varepsilon_0\varepsilon_{\mathrm{st}}\left[\mathrm{d}\left(1/C^2\right)/\mathrm{d}V\right]} \quad (2)$$

Where ε_0 and ε_{st} are the vacuum dielectric constant and low frequency dielectric constant, respectively. The values of d(1/C^2)/dV were obtained from six-order polynomial fit to 1/C^2-V data. The 1/C^2-V curves were shown in Fig. 6(b). The six-order polynomial fitted results of PMN-PT thin

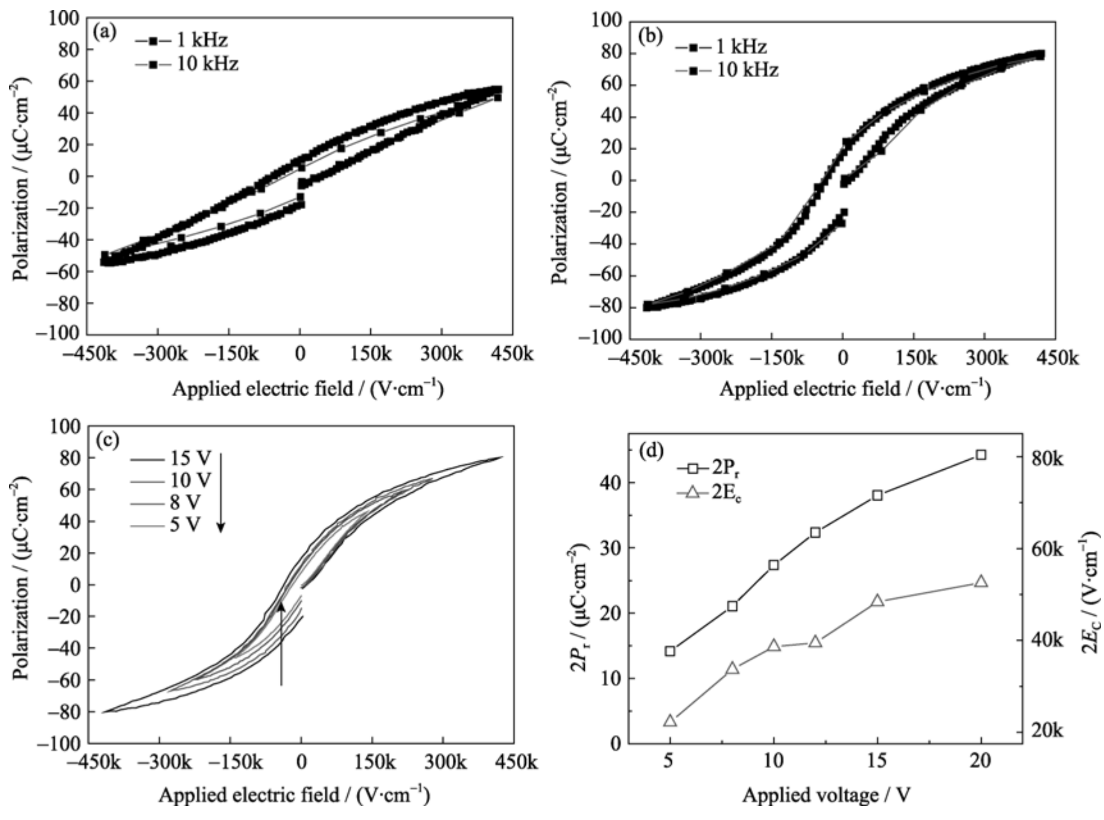

Fig. 5 *P-E* hysteresis loops of the PMN-PT thin films prepared (a) without and (b) with oxygen plasma assisted, (c) *P-E* characteristics of the PMN-PT thin film prepared with oxygen plasma assisted under different applied electric field, (d) the variety of remnant polarization and coercive field with applied voltage

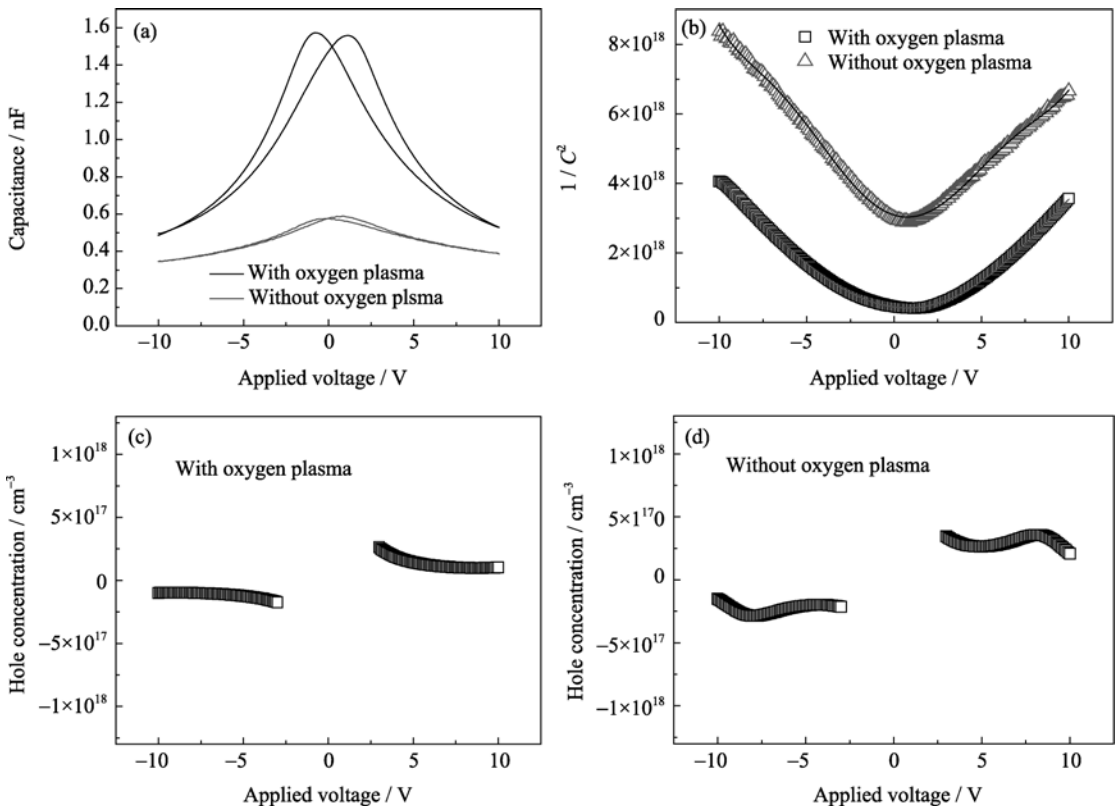

Fig. 6　(a) *C*-*V* characteristics and (b) $1/C^2$-*V* plots of the PMN-PT thin films, Hole concentration estimations of PMN-PT thin films prepared (c) with and (d) without oxygen plasma assisted

films to $1/C^2$-*V* data also displayed in Fig. 6(b). As can be seen from Fig. 6(c) and (d), the Hole concentrations of the PMN-PT thin films prepared without and with oxygen plasma assisted estimated using Eq.(2) are about 2.1×10^{17} cm^{-3} and 1.2×10^{17} cm^{-3}, respectively. Both films were prepared at the same temperature and deposition rates, thus, the higher Hole concentration of the PMN-PT thin film prepared without oxygen plasma assisted probably resulted from the loose microstructure and the relative poor crystalline quality. These results indicate lower Hole concentration can be achieved by employing oxygen plasma assisted during the PLD process.

3　Conclusions

Highly (001)-oriented PMN-PT ferroelectric thin film was deposited on Ir/$SrTiO_3$/TiN/Si (001) substrate by pulsed laser deposition method employing plasma oxygen source. Due to the high activity of plasma oxygen molecules, PMN-PT thin film with high crystalline quality and compact microstructure was obtained under low oxygen pressure. Excellent dielectric and ferroelectric properties were observed in this PMN-PT film. Therefore, the control of oxygen partial pressure is the key issue to deposit the high quality PMN-PT thin films.

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氧等离子体辅助脉冲激光沉积法制备 PMN-PT 薄膜的微观结构和电学性能

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摘 要: 采用氧等离子体辅助脉冲激光沉积方法(PLD)在硅衬底上, 制备出高度(001)取向的钙钛矿相结构钛铌镁酸铅(PMN-PT)薄膜. 研究了氧等离子体辅助对 PMN-PT 薄膜相结构、微观形貌和电学性能的影响. 结果表明, 通过在薄膜沉积过程中引入高活性的氧等离子, 可以有效地提高 PMN-PT 薄膜的结晶质量和微观结构. 未采用氧等离子体辅助 PLD 方法制备 PMN-PT 薄膜的介电常数(10 kHz)和剩余极化($2P_r$)分别为 1484 和 18 μC/cm^2, 通过采用氧等离子体辅助, 其介电常数和剩余极化分别提高至 3012 和 38 μC/cm^2.

关 键 词: 脉冲激光沉积法; PMN-PT 薄膜; 微观结构; 电学性能

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