

柔性 $\text{Pb}_{0.99}\text{Sm}_{0.01}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.68}\text{Ti}_{0.32}\text{O}_3$ 弛豫铁电薄膜储能特性

吕盼盼¹, 石长清¹, 辛 乐³, 战 行¹, 张书志¹, 王 佳¹, 李瑞航¹, 李存成¹,
任路超¹, 杨长红⁴, 张明伟^{1,2}, 程 新⁴

(1. 山东理工大学材料科学与工程学院, 山东 淄博 255000; 2. 山东理工大学分析测试中心, 山东 淄博 255000; 3. 淄博师范高等专科学校数理系, 山东 淄博 255130; 4. 济南大学, 山东省建筑材料制备与测试技术重点实验室, 济南 250022)

摘 要: 弛豫铁电薄膜电容器因具有细长电滞回线和高能量转化效率成为介电储能应用的理想选择。本工作采用溶胶凝胶法在沉积有 LaNiO_3 缓冲层的云母基底上直接制备了柔性 $\text{Pb}_{0.99}\text{Sm}_{0.01}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.68}\text{Ti}_{0.32}\text{O}_3$ (PSMNT) 薄膜, 系统研究了柔性 PSMNT 膜的微观结构、介电、铁电和储能性能。X 射线衍射结果表明薄膜样品为单一钙钛矿相。扫描电子显微镜结果显示薄膜的晶粒尺寸均匀且致密。在极化特性方面, 所制备的柔性 PSMNT 薄膜因具有弛豫性, 其电滞回线呈现出纤细束腰特征, 在外加电场 2468 kV/cm 下, 其最大饱和极化为 $74.5\text{ }\mu\text{C/cm}^2$, 剩余极化为 $16.4\text{ }\mu\text{C/cm}^2$ 。薄膜电容器击穿前最大可释放能量密度和储能效率分为 40.7 J/cm^3 和 70%, 并且表现出较好的频率(1~20 kHz)和温度(25~120 °C)稳定性。此外, 样品借助云母衬底可实现优异的可弯折性, 在弯曲半径 R 低至 2 mm 和弯曲疲劳循环 1 000 次($R=4\text{ mm}$)后, 其储能性能仍可保持。此研究表明以云母为基底的 PSMNT 弛豫薄膜在柔性储能领域具有很大的应用潜力。

关键词: 铌镁酸铅钛酸铅基薄膜; 弛豫铁电体; 介电储能; 柔性

中图分类号: TB34 文献标志码: A 文章编号: 0454-5648(2024)04-1301-09

网络出版时间: 2024-03-11



能源在社会发展中占据着关键地位, 介电电容器作为功率型储能器件, 因其高功率密度和快充放电速率, 已被广泛应用于脉冲功率系统中^[1-3]。近年来, 随着轻质化、柔性化及紧凑型电子产品需求量的增大^[4], 能够提供高能量、高功率的柔性储能器件已变得不可或缺。然而, 传统的柔性高分子聚合物薄膜介电常数较低($\epsilon_r < 10$), 导致所制备的电容器能量密度偏低($W_{\text{rec}} < 3\text{ J/cm}^3$)^[5-6], 在实际应用中严重受限。因此, 开发具有高储能特性的柔性电介质材料具有重要意义。

介质材料在外加电场下的极化行为可用极化-电场(P - E)电滞回线来描述。在众多不同极化类型的电介质材料中, 弛豫型铁电体因其内部纳米畴间相互耦合作用弱, 表现出瘦长型电滞回线, 因此被认为是极具潜力的候选储能材料^[7-8]。二元固溶体 $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $x\text{PbTiO}_3$ (PMNT) 是一种典型

的弛豫型铁电体系, 当组分在准同型相界($x \approx 0.35$)附近时具有高介电常数和压电系数, 在压电传感领域备受青睐^[9-10]。同时, 弛豫铁电体纤细的 P - E 电滞回线赋予 PMNT 较低的剩余极化和矫顽场, 这意味着 PMNT 在放电过程中能释放出更多的能量, 因此近年来关于 PMNT 薄膜储能性能的研究也受到了越来越多的关注。例如, Wang 等^[11]在 0.9PMN-0.1PT 体系中获得了高能量密度 31.3 J/cm^3 ; Xia 等^[12]在 La 掺杂的 0.88PMN-0.12PT 薄膜中得到的储能密度为 25.2 J/cm^3 ; Park 等^[13]在纳米级晶粒铁电体 0.65PMN-0.35PT 厚膜中获得的能量密度为 35 J/cm^3 。2020 年, Kim 等^[14]采用离子轰击弛豫铁电薄膜 $0.68\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - 0.32PbTiO_3 产生本征点缺陷来提高储能特性, 其能量密度可达 133 J/cm^3 , 这是 PMNT 基薄膜材料迄今为止报道出的最高储能密度。然而, 离子轰击辅助方法并非是调控铁电薄膜

收稿日期: 2023-09-29。 修订日期: 2023-11-03。

基金项目: 国家自然科学基金青年科学基金(52302145); 山东省自然科学基金青年基金(ZR2023QE126); 国家自然科学基金面上项目(51972144)。

第一作者: 吕盼盼(1990—), 女, 博士, 讲师。

通信作者: 张明伟(1982—), 男, 博士, 教授。

Received date: 2023-09-29. Revised date: 2023-11-03.

First author: LV Panpan (1990—), female, Ph.D., Lecture.

E-mail: lvpp@sdu.edu.cn

Correspondent author: ZHANG Mingwei (1982—), male, Ph.D., Professor.

E-mail: zmw@sdu.edu.cn

储能性能的常规手段,限制了其进一步发展。

此外,随着电子产品向小型化、可穿戴方向发展,兼具高储能特性和柔韧性的储能器件备受关注,然而 PMNT 薄膜其高达 600 °C 的结晶温度令传统柔性聚合物基底望而却步^[15]。最近,也有关于柔性 PMNT 储能薄膜的报道,例如, Peddigari 等^[16]利用无机物基激光发射工艺将沉积于蓝宝石晶片上的 0.9PMN-0.1PT 结晶薄膜转移至聚对苯二甲酸乙二醇酯聚合物柔性衬底上,获得了储能密度为 10.7 J/cm³ 的柔性 PMNT 基储能薄膜。但转移工序较复杂且薄膜性能在复杂工艺环境下易发生退化。研究者们也尝试用其他柔性化方式来实现无机薄膜的柔性化,如刻蚀法、机械减薄法、直接生长法等^[17–20]。利用耐高温层状硅酸盐云母材料作为衬底可以直接构建无机柔性功能单元,如刘俊明等^[20]通过脉冲激光沉积技术在以 SrRuO₃ 为缓冲层的云母基底上外延生长了 BaTi_{0.95}Co_{0.05}O₃ 薄膜,其阻变性能受弯曲曲率影响较小,为无机功能薄膜的柔性化提供了新的途径。

鉴于 $x > 0.4$ 时, PMNT 将成为正常铁电体,设计 0.68PMN-0.32PT 二元固溶体系。通过引入钙钛矿氧化物 LaNiO₃ (LNO)缓冲层促进薄膜的生长,同时掺入微量镧系元素 Sm (1%, 摩尔分数),降低漏电流,提高击穿场强,显著提升薄膜的储能密度和效率。借助二维云母作为柔性载体平台实现薄膜的柔性化。系统研究了柔性 Pb_{0.99}Sm_{0.01}(Mg_{1/3}Nb_{2/3})_{0.68}Ti_{0.32}O₃ (PSMNT)薄膜的晶体结构、微观形貌与介电、铁电、储能性能以及耐弯折性,为 PMNT 基弛豫铁电材料在柔性介电储能领域中的应用提供了参考。

1 实验

1.1 样品制备

采用溶胶凝胶法制备 PSMNT 和 LNO 前驱体溶液。PSMNT: 将原料乙醇铌[Nb(OC₂H₅)₅, 麦克林, 99.5%]溶解到乙二醇甲醚中,得到含铌溶液。将钛酸四丁酯[Ti(OC₄H₉)₄, 麦克林, 99.0%]溶解到乙酰丙酮中,得到稳定的钛溶液。将化学计量 1.09:0.227:0.01 的醋酸铅[Pb(CH₃COO)₂·3H₂O, 麦克林, 99.5%]、醋酸镁[Mg(CH₃COO)₂·4H₂O, 麦克林, 99.0%]和硝酸钐[Sm(NO₃)₃·6H₂O, 麦克林, 99.9%]溶解于总体积为 20 mL 醋酸(CH₃COOH, 麦克林, 99.5%)和乙二醇甲醚(C₃H₈O₂, 麦克林, 99.0%)混合溶剂中,醋酸和乙二醇甲醚的体积比为 2:1。铅过量摩尔比为 10%,以弥补在薄膜制备过程中铅的挥发。向铅、

镁和钐混合溶液中依次加入铌、钛溶液,配制得到浓度为 0.2 mol/L 的 PSMNT 前驱体溶液。LNO: 将醋酸镍[Ni(CH₃COO)₂·4H₂O, 麦克林, 99.0%]和硝酸镧[La(NO₃)₃·6H₂O, 麦克林, 99.0%]按化学计量比 1:1 溶于 20 mL 乙二醇甲醚中,得到 0.1 mol/L 的 LNO 前驱体溶液。

实验用柔性云母(Mica)衬底通过简单的机械减薄而获取,将云母衬底置于去离子水中用刀片在其边缘插入进行机械解理,多次剥离后云母片厚度可低至 15 μm 进而展现出良好的柔韧性。以柔性云母为载体平台,首先将 LNO 前驱体溶液旋涂至衬底表面,并置于快速退火炉中退火 2 min,退火温度为 750 °C。然后在 LNO 表面再旋涂 PSMNT 前驱体溶液,在快速退火炉内 700 °C 温度下进行退火处理,多次重复上述匀胶和热处理过程,直至得到所需厚度的 LNO 缓冲层和 PSMNT 薄膜样品。为了测试样品的电学性能和储能特性,以导电氧化物 LNO 缓冲层作为底电极,顶电极则采用真空溅射法制备 Au 点电极,其直径为 200 μm。

1.2 样品表征

采用德国布鲁克公司的 D8 Advance 型 X 射线衍射仪(XRD)对薄膜样品的物相进行分析,测试条件: 2θ 角度扫描范围为 20°~60°,扫描速率为 2 (°)/min; 采用美国赛默飞 FEI Apreo 型场发射扫描电子显微镜(SEM)观察样品的微观形貌; 利用美国 Radiant Precision Multiferroic 型铁电测试仪测试样品的电滞回线并据此计算样品的储能密度及储能效率; 利用美国安捷伦 E4980A 型阻抗分析仪和英国 Linkam 高低温探针台测试样品的介电性能。

2 结果与讨论

2.1 物相结构

图 1a 为 PSMNT 薄膜的制备过程,在机械减薄的云母衬底上通过旋涂和层层退火工艺分别沉积 LNO 缓冲层和 PSMNT 功能层,高温结晶后得到柔性 PSMNT/LNO/Mica 单元,中间插图为样品的实物照片。图 1b 为 PSMNT/LNO/Mica 和纯 Mica 衬底在 20°~60°范围内的 XRD 图谱。由图 1b 可见,薄膜样品为单一的钙钛矿结构,无杂相生成。此外,从 XRD 结果可以看出薄膜是以(100)择优取向为主的多晶取向,这主要是由于 LNO 缓冲层的引入有利于 PSMNT 薄膜(100)取向的晶粒生长,也进一步证明了 PSMNT 薄膜能够在云母基底上充分结晶。

2.2 微观形貌

图 2a 和图 2b 分别为 PSMNT 薄膜和 LNO 缓冲层的表面 SEM 照片。由图 2 可见, PSMNT 和 LNO 薄膜表面光滑、无明显裂纹, 局部孔洞的形成是有

机溶剂挥发所引起的。相较于 LNO 缓冲层而言, PSMNT 薄膜表面晶粒较大且呈现出致密的结构。图 2c 为 PSMNT/LNO/Mica 结构的 FESEM 断面形貌, LNO 种子层和 PSMNT 功能层之间由于晶粒尺

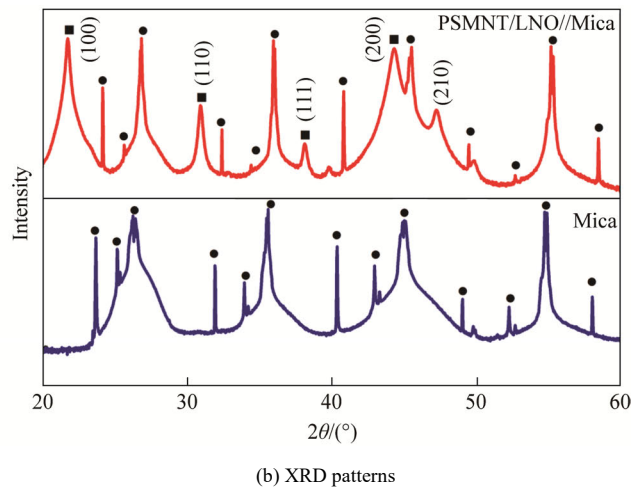
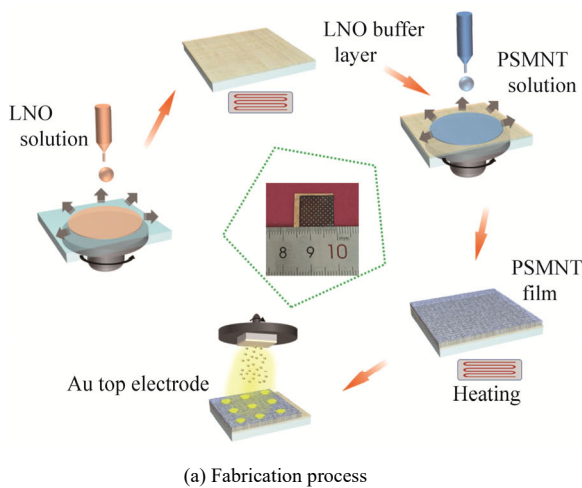


图 1 PSMNT 薄膜的制备流程图和 XRD 谱

Fig. 1 Schematic diagrams and X-ray diffraction patterns of the PSMNT film

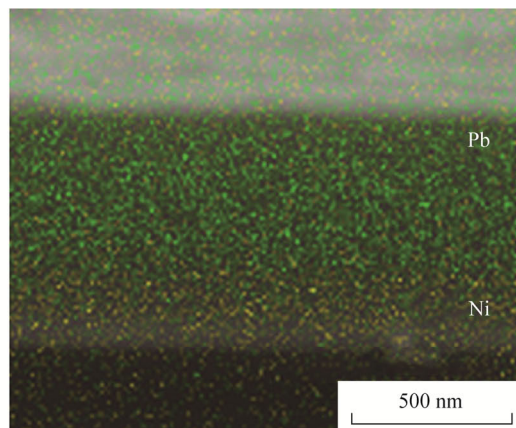
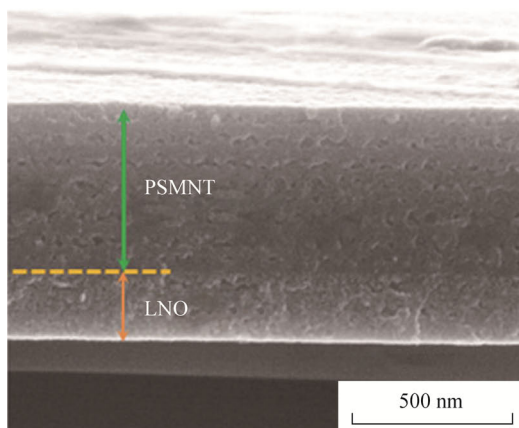
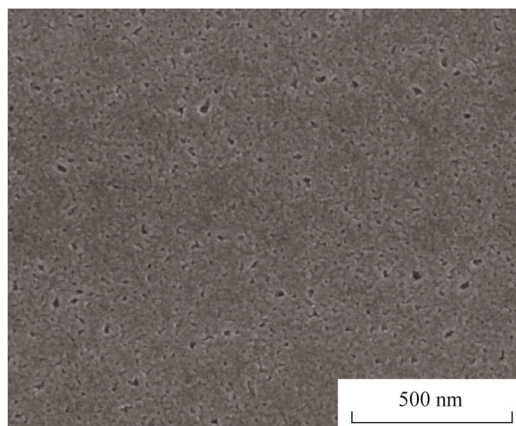
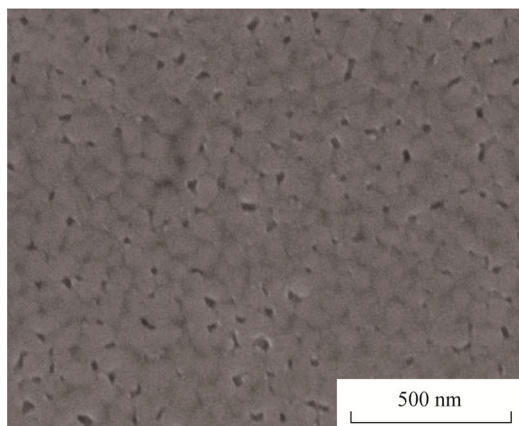


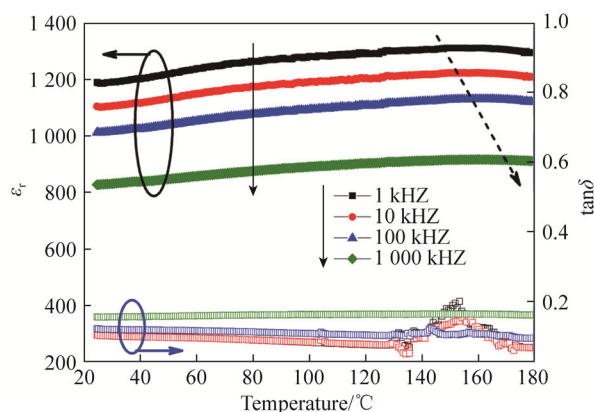
图 2 PSMNT 薄膜和 LNO 缓冲层的 SEM 图片和 EDS 扫描图

Fig. 2 SEM images and EDS elemental mapping of the PSMNT/LNO/Mica element

寸的差异存在较明显分界线。PSMNT 膜和 LNO 缓冲层的厚度分别约为 500 nm 和 200 nm。此外,从截面特征元素 EDS 面扫描结果(图 2d)可以更清晰地分辨出 LNO 缓冲层与 PSMNT 膜层的界面。

2.3 介电性能

图 3a 为 PSMNT 薄膜在不同温度(25~180 °C)及不同频率(1~1 000 kHz)下的介电常数(ϵ_r)和介电损耗($\tan\delta$)的变化曲线。由图 3a 可见,薄膜的介电常数在整个室温至 180 °C 温度区间内随温度变化缓慢,介电常数峰展宽。而且随着频率的增加,介电常数峰值向高温方向移动,表现出明显的频率色散关系,

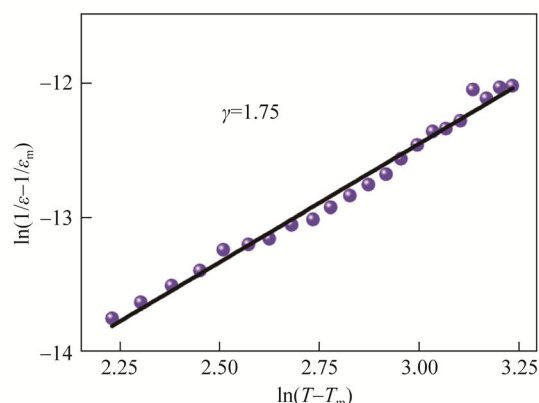


(a) Dielectric temperature spectra of the PSMNT film

这是弛豫铁电体的典型特征之一^[21]。采用修正的 Curie-Weiss 方程对 ϵ_r 随温度的变化关系进行分析,修正后的 Curie-Weiss 方程如下:

$$\ln(1/\epsilon - 1/\epsilon_{\max}) = \gamma \ln(T - T_{\max}) + C' \quad (1)$$

其中: $\epsilon_{\max}$ 为 $T=T_{\max}$ 时的介电常数; γ 为弥散指数。对于弥散型铁电相变, γ 在 1 和 2 之间, γ 值越大代表相变的弥散程度越大^[22]。拟合的结果见图 3b, 沉积于 Mica 基底上的 PSMNT 薄膜的弥散指数 γ 为 1.75, 说明薄膜中离子分布无序程度较高, 进一步证实了其弛豫特性, 这也是 PSMNT 材料可用于介电储能的原因之一。



(b) Diffuseness parameter γ for PSMNT film

图 3 PSMNT 薄膜在不同频率下的介电特性

Fig. 3 Dielectric properties of PSMNT film at different testing frequencies

2.4 极化与储能特性

图 4a 为 PSMNT 薄膜的电滞回线(P - E 曲线), 可以看出, PSMNT 薄膜的电滞回线在不同电场下始终保持纤细束腰特征, 在外加电场 2 468 kV/cm 下, 其最大饱和极化 $P_{\max}$ 为 74.5 $\mu\text{C}/\text{cm}^2$, 剩余极化 P_r 为 16.4 $\mu\text{C}/\text{cm}^2$ 。而相同条件下制备的未掺杂 PMNT 薄膜其 P - E 回线只能在较低的电场下具有细长特征, 高电场下转变为宽胖型(图 4b), 不饱和行为的出现主要是漏电流所导致的。从两种薄膜漏电流密度随电场的变化曲线(图 4c)也能看出掺杂镧系元素 Sm 能够有效降低薄膜的漏电流, 这主要是由于施主 Sm^{3+} 取代 Pb^{2+} 可以减少氧化位, 从而提高薄膜绝缘性^[23]。为了表征薄膜的击穿场强(E_b), 根据 Weibull 分布函数, 即

$$X_i = \ln(E_i) \quad (2)$$

$$Y_i = \ln(-\ln(1 - i / (n + 1))) \quad (3)$$

$$E_1 \leq E_2 \leq \dots \leq E_i \dots \leq E_n \quad (4)$$

其中: E_i 为每个样品对应的击穿场强; i 为样品序号;

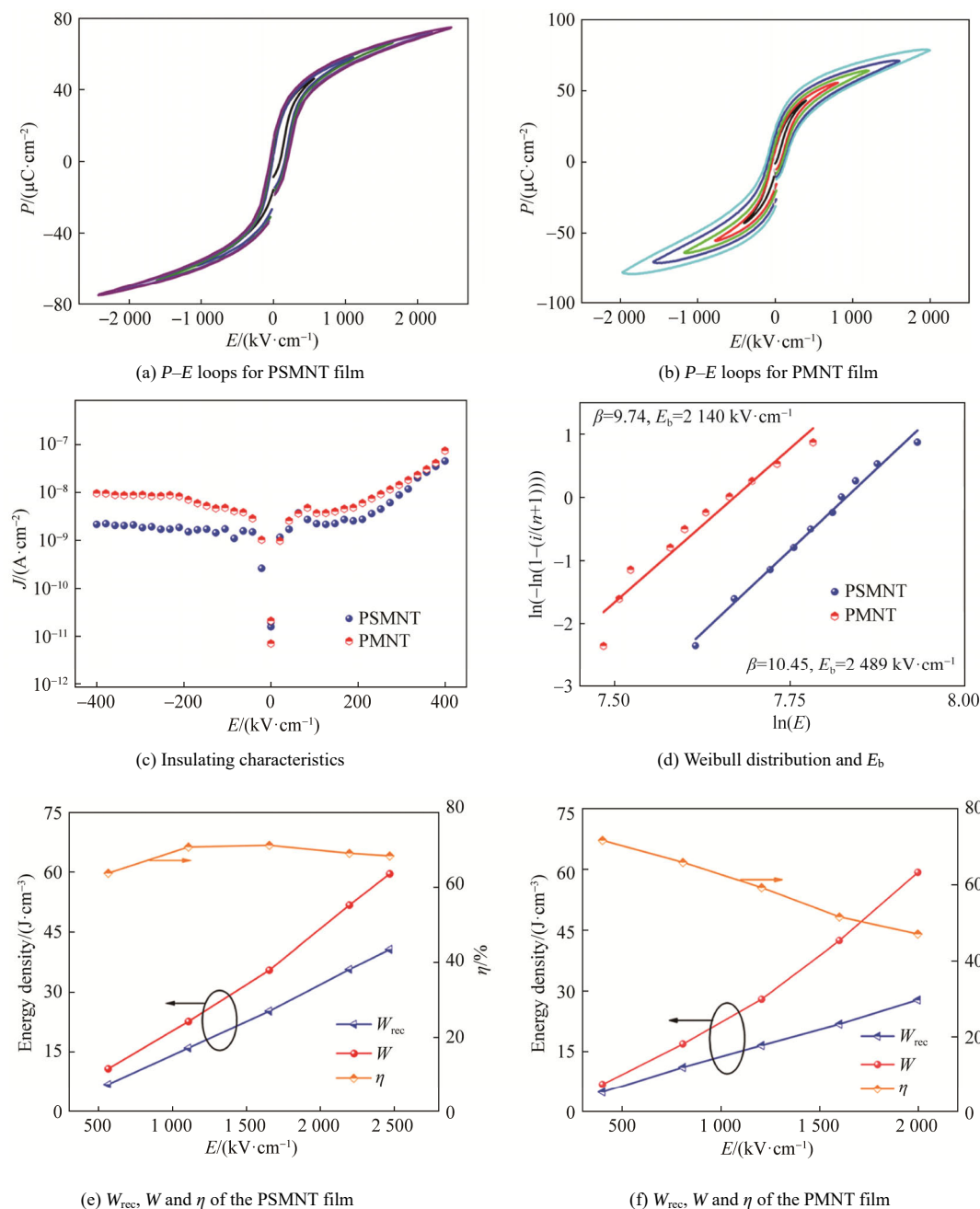
n 为样品总数。根据公式, 拟合得到 PSMNT 和 PMNT 样品的击穿场强 E_b 如图 4d 所示, 其平均值分别为 2 489 kV/cm 和 2 140 kV/cm。根据 P - E 曲线计算可释放储能密度 W_{rec} , 总储能密度 W 和储能效率 η , 计算公式如下:

$$W_{\text{rec}} = \int_{P_r}^{P_{\max}} E dP \quad (5)$$

$$W = \int_0^{P_{\max}} E dP \quad (6)$$

$$\eta = \frac{W_{\text{rec}}}{W} \quad (7)$$

其中: E 为外加电场场强; $P_{\max}$ 为最大极化值, P_r 为剩余极化值; P 为极化强度。利用式(5)~式(7)分别计算出不同外加电场强度下 PSMNT 和 PMNT 样品的 W_{rec} 、 W 和 η , 结果见图 4e 和图 4f。由图 4e 和图 4f 可见, 随着电场强度从 564 kV/cm 增加至 2 468 kV/cm, PSMNT 薄膜的 W_{rec} 从 6.9 J/cm³ 增至 40.7 J/cm³, 呈现线性增长的趋势, 且 η 维持在 70%, 具有良好的储能效率稳定性。而未掺杂的 PMNT 薄膜由于其



P is the polarization. E is the applied electric field. W_{rec} is the recoverable energy storage density. W is the whole stored energy density. η is the energy storage efficiency. E_b is the electric breakdown field.

图 4 PSMNT 和 PMNT 薄膜的铁电性和储能特性

Fig. 4 Ferroelectric characteristics and energy storage performances of PSMNT and PMNT films

漏电严重, 击穿场强较低, 造成有效储能密度最大值仅为 $27.8 \text{ J}/\text{cm}^3$, 且储能效率由于回滞增大逐渐降低。

图 5 是 PSMNT/LNO/Mica 在不同频率(1~20 kHz)和不同温度(25~120 °C)下的电滞回线和储能性能。由图 5a 和图 5b 可见, 薄膜的储能密度和效率在 1~20 kHz 范围内具有良好的稳定性, 可释放储能密度 W_{rec} 和储能效率 η 的变化率分别为 9% 和 7%。图 5c 为 PSMNT 薄膜在升温环境下的 $P-E$ 曲线, 测试温度范围为

25~120 °C。由图可见, 在变温测试下, 薄膜的 $P-E$ 曲线形状变化不大, W_{rec} 在 $25.3\sim 26.5 \text{ J}/\text{cm}^3$ 范围内波动, 储能效率在 70%~76% 范围内波动, 说明该储能薄膜在室温至 120 °C 具有良好的温度稳定性, 可应用于较宽温度范围内的脉冲功率电容器的制作。

鉴于云母在厚度为 100 nm 时其弯曲半径可达 0.1 mm 以下, 沉积于 LNO/Mica 上的 PSMNT 薄膜样品可展现出优异的可弯曲性能, 由图 6 可见, 即

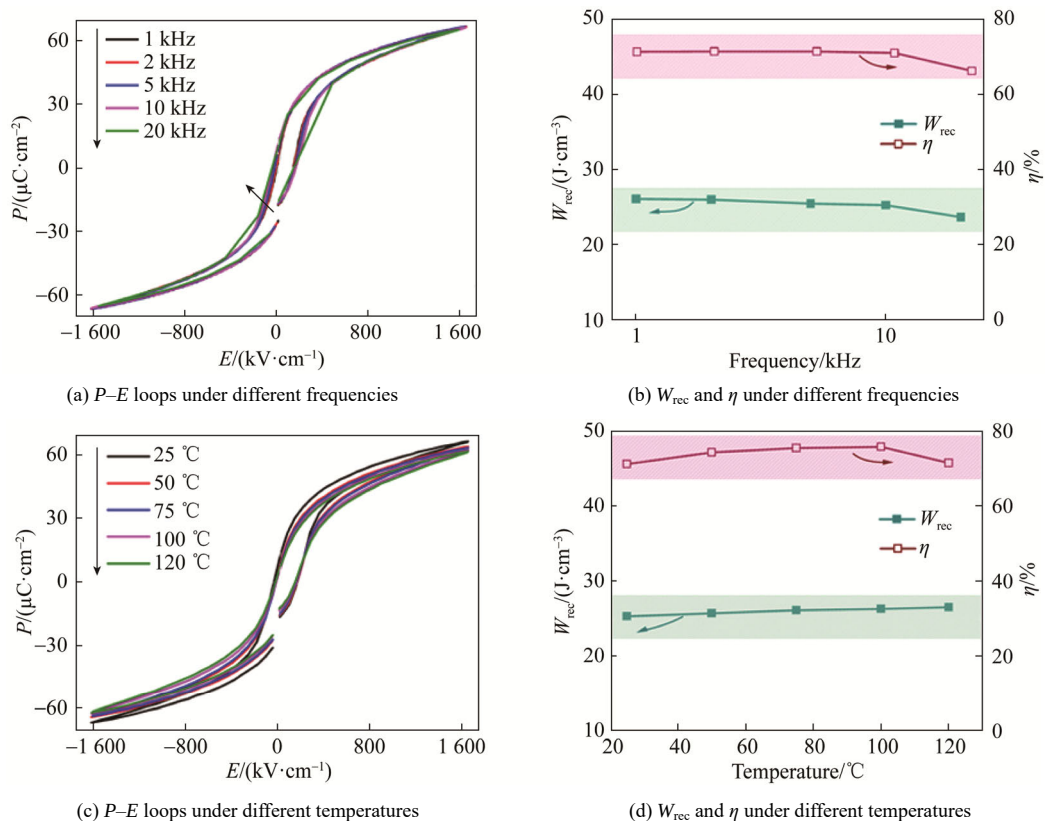
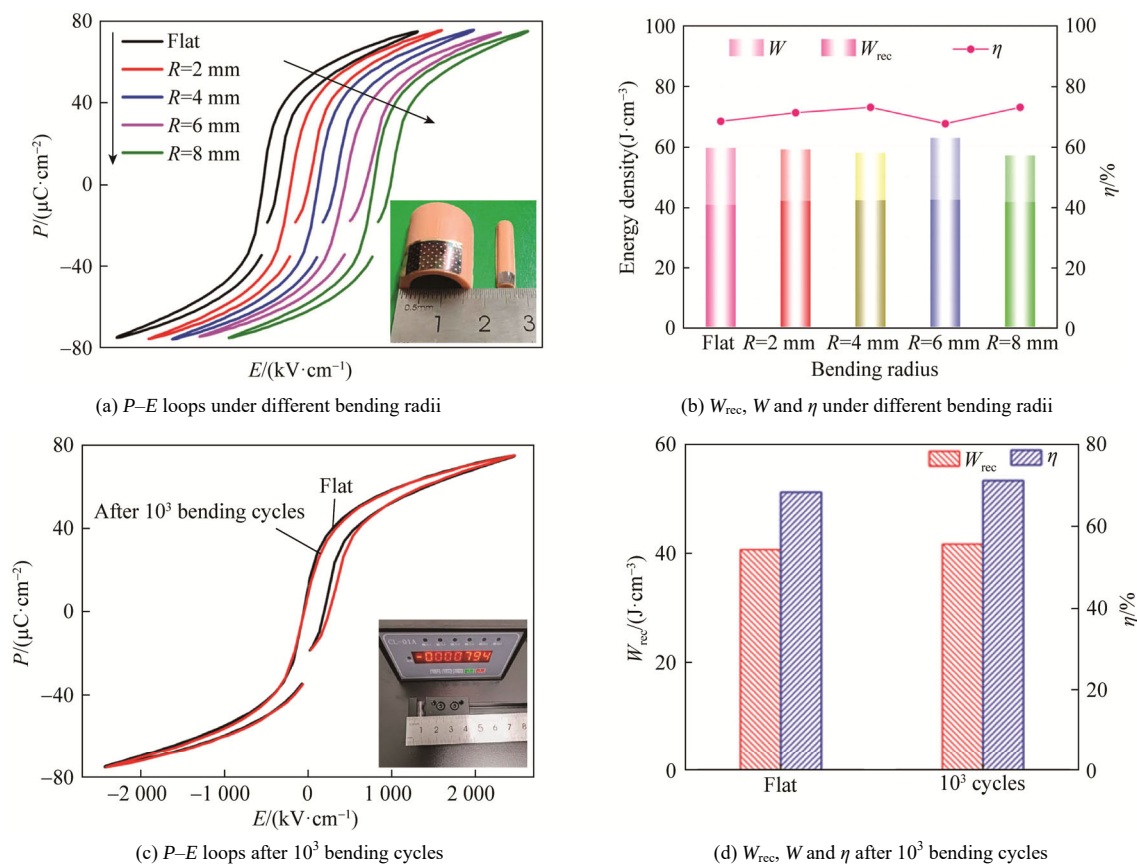
图5 PSMNT/LNO/Mica 在不同频率和温度下的 P - E 电滞回线和储能性能Fig. 5 Frequency and temperature dependent P - E loops and W_{rec} and η of PSMNT/LNO/Mica

图6 PSMNT/LNO/Mica 弯曲状态下的储能特性

Fig. 6 W , W_{rec} and η of PSMNT/LNO/Mica under different bending conditions

使薄膜的弯曲半径 R 低至 2 mm, 其 P - E 回线仍与原始平整状态几乎重合, 可释放储能密度和效率的波动性较小。此外, 在曲率半径 $R=4$ mm 状态下, 薄膜经历 1 000 次重复弯曲后样品仍具有与平整样品一致的储能特性, 表明其在弯折状态下具有出色的鲁棒性, 可满足柔性储能器件的需求。

图 7 为所制备的柔性 PSMNT 薄膜与先前报道的 PMNT 和 PZT 基薄膜材料储能性能的对

图。从图中可见, PSMNT 薄膜的可释放储能密度和效率相较于硬质衬底上不同组分 PMNT 和 PZT 基薄膜而言处于较高的水平^[11-14, 16, 24-31]。此外, 与生长转移的 0.9PMN-0.1PT 薄膜^[16]和同样沉积在 Mica 衬底上的柔性 PZT 基薄膜相比^[31] (红色框选), PSMNT 薄膜的可释放储能密度也相对较高, 进一步说明了 PSMNT 薄膜在柔性储能电容器领域具有优势。

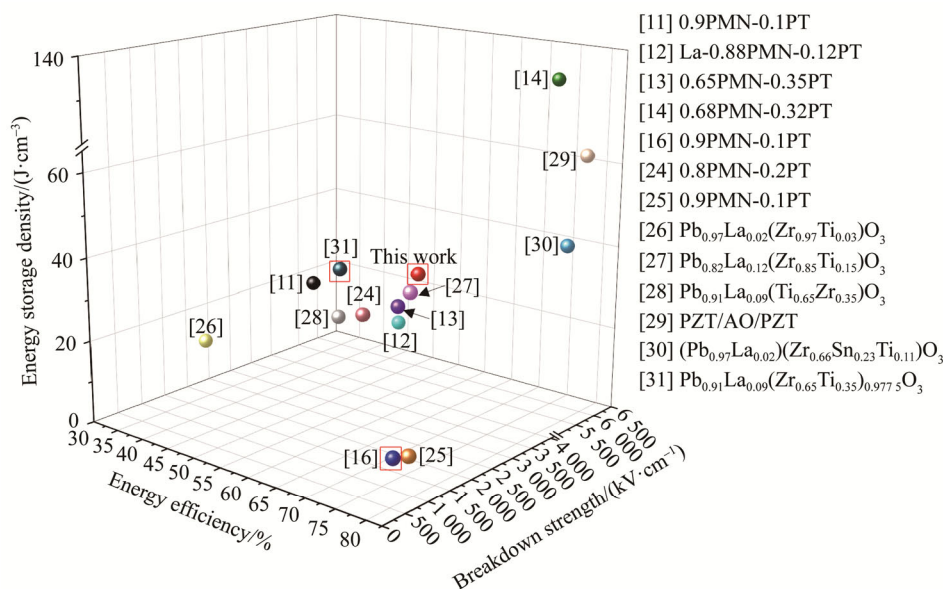


图 7 柔性 PSMNT 薄膜与先前报道的 PMNT 和 PZT 基薄膜介电储能性能的对

Fig. 7 A comparison of the W_{rec} and η of the flexible PSMNT film capacitor reported in this study and a number of PMNT and PZT based film capacitors reported previously^[11-14, 16, 24-31]

3 结论

沉积在柔性云母衬底上的弛豫 PSMNT 薄膜具有单一的钙钛矿结构, 晶粒尺寸均匀且结构致密。同时氧化物 LNO 缓冲层的引入可以促进(100)取向 PSMNT 薄膜的生长, 而镧系元素 Sm 的掺入有助于降低漏电流, 提高击穿场强, 使得薄膜的储能密度和效率显著提升。在 2 468 kV/cm 电场下, 储能密度为 40.7 J/cm³, 储能效率为 70%。在测试频率为 1~20 kHz 和测试温度为 25~120 °C 时, 表现出较稳定的储能密度和效率。此外, 薄膜电容器表现出优越的耐弯折性, 在弯曲半径 $R=2$ mm 和弯曲疲劳循环 1 000 次($R=4$ mm)时, 其储能性能仍可保持, 表明柔性 PSMNT 薄膜在柔性储能领域具有较好的潜在应用价值。

参考文献:

[1] YANG L T, KONG X, LI F, et al. Perovskite lead-free dielectrics for

energy storage applications[J]. Prog Mater Sci, 2019, 102: 72-108.

- [2] WANG G, LU Z L, LI Y, et al. Electroceramics for high-energy density capacitors: Current status and future perspectives[J]. Chem Rev, 2021, 121(10): 6124-6172.
- [3] QIAN J, LI G H, ZHU K, et al. High energy storage performance and large electrocaloric response in $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ - $\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ thin films[J]. ACS Appl Mater Interfaces, 2022, 14(48): 54012-54020.
- [4] LI L, WU Z, YUAN S A, et al. Advances and challenges for flexible energy storage and conversion devices and systems[J]. Energy Environ Sci, 2014, 7(7): 2101.
- [5] 杨敏铮, 江建勇, 沈洋. 高能量密度介电储能材料研究进展[J]. 硅酸盐学报, 2021, 49(7): 1249-1262.
- [6] YANG Minzheng, JIANG Jianyong, SHEN Yang. J Chin Ceram Soc, 2021, 49(7): 1249-1262.
- [7] MA R, BALDWIN A F, WANG C C, et al. Rationally designed polyimides for high-energy density capacitor applications[J]. ACS Appl Mater Interfaces, 2014, 6(13): 10445-10451.
- [8] LV P P, QIAN J, YANG C H, et al. 4-inch ternary BiFeO_3 - BaTiO_3 - SrTiO_3 thin film capacitor with high energy storage performance[J]. ACS Energy Lett, 2021, 6(11): 3873-3881.
- [9] HAO X H. A review on the dielectric materials for high energy-storage application[J]. J Adv Dielect, 2013, 3(1): 1330001.
- [10] LI F, LIN D B, CHEN Z B, et al. Ultrahigh piezoelectricity in

- ferroelectric ceramics by design[J]. *Nat Mater*, 2018, 17(4): 349–354.
- [10] LI F, CABRAL M J, XU B, et al. Giant piezoelectricity of Sm-doped $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 single crystals[J]. *Science*, 2019, 364(6437): 264–268.
- [11] WANG X L, ZHANG L, HAO X H, et al. High energy-storage performance of $0.9\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - 0.1PbTiO_3 relaxor ferroelectric thin films prepared by RF magnetron sputtering[J]. *Mater Res Bull*, 2015, 65: 73–79.
- [12] XIA X J, SUN H J, SUI H T, et al. Investigation on high energy storage properties in La^{3+} -doped 0.88PMN - 0.12PT relaxor ferroelectric films[J]. *Surf Interfaces*, 2022, 28: 101670.
- [13] PARK C K, LEE S, LIM J H, et al. Nano-size grains and high density of 65PMN - 35PT thick film for high energy storage capacitor[J]. *Ceram Int*, 2018, 44(16): 20111–20114.
- [14] KIM J, SAREMI S, ACHARYA M, et al. Ultrahigh capacitive energy density in ion-bombarded relaxor ferroelectric films[J]. *Science*, 2020, 369(6499): 81–84.
- [15] ZHAO Y Y, LI X L, HU G D, et al. Low-temperature preparation of self-polarized $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 films on well crystallized LaNiO_3 electrodes[J]. *J Alloys Compd*, 2013, 577: 606–609.
- [16] PEDDIGARI M, PARK J H, HAN J H, et al. Flexible self-charging, ultrafast, high-power-density ceramic capacitor system[J]. *ACS Energy Lett*, 2021: 1383–1391.
- [17] PARK S I, AHN J H, FENG X E, et al. Theoretical and experimental studies of bending of inorganic electronic materials on plastic substrates[J]. *Adv Funct Materials*, 2008, 18(18): 2673–2684.
- [18] HWANG G T, PARK H, LEE J H, et al. Self-powered cardiac pacemaker enabled by flexible single crystalline PMN - PT piezoelectric energy harvester[J]. *Adv Mater*, 2014, 26(28): 4880–4887.
- [19] YEO H G, MA X K, RAHN C, et al. Efficient piezoelectric energy harvesters utilizing (001) textured bimorph PZT films on flexible metal foils[J]. *Adv Funct Materials*, 2016, 26(32): 5940–5946.
- [20] YANG Y X, YUAN G L, YAN Z B, et al. Flexible, semitransparent, and inorganic resistive memory based on $\text{BaTi}_{0.95}\text{Co}_{0.05}\text{O}_3$ film[J]. *Adv Mater*, 2017, 29(26): 1700425.
- [21] CUI C W, PU Y P. Effect of Sn substitution on the energy storage properties of 0.45SrTiO_3 - $0.2\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ - 0.35BaTiO_3 ceramics[J]. *J Mater Sci*, 2018, 53(13): 9830–9841.
- [22] SHEN Z B, WANG X H, LUO B C, et al. BaTiO_3 - BiYbO_3 perovskite materials for energy storage applications[J]. *J Mater Chem A*, 2015, 3(35): 18146–18153.
- [23] ZHANG S J, LI F. High performance ferroelectric relaxor- PbTiO_3 single crystals: Status and perspective[J]. *J Appl Phys*, 2012, 111(3): 031301.
- [24] WANG X L, ZHANG L W, HAO X H, et al. Dielectric properties and energy-storage performances of $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $x\text{PbTiO}_3$ relaxor ferroelectric thin films[J]. *J Mater Sci Mater Electron*, 2015, 26(12): 9583–9590.
- [25] SADL M, CONDURACHE O, BENCAN A, et al. Energy-storage-efficient $0.9\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - 0.1PbTiO_3 thick films integrated directly onto stainless steel[J]. *Acta Mater*, 2021, 221: 117403.
- [26] LIU Y Y, WANG Y, HAO X H, et al. Preparation and energy-storage performance of PLZT antiferroelectric thick films via sol-gel method[J]. *Ceram Int*, 2013, 39: S513–S516.
- [27] ZHAO Y, HAO X H, ZHANG Q. Energy-storage properties and electrocaloric effect of $\text{Pb}(1-3x/2)\text{La}_x\text{Zr}_{0.85}\text{Ti}_{0.15}\text{O}_3$ antiferroelectric thick films[J]. *ACS Appl Mater Interfaces*, 2014, 6(14): 11633–11639.
- [28] HAO X H, WANG Y, YANG J C, et al. High energy-storage performance in $\text{Pb}_{0.91}\text{La}_{0.09}(\text{Ti}_{0.65}\text{Zr}_{0.35})\text{O}_3$ relaxor ferroelectric thin films[J]. *J Appl Phys*, 2012, 112(11): 114111.
- [29] ZHANG T D, LI W L, ZHAO Y, et al. Structure-property relationships: High energy storage performance of opposite double-heterojunction ferroelectricity-insulators[J]. *Adv Funct Materials*, 2018, 28(10): 1706211.
- [30] LIN Z J, CHEN Y, LIU Z, et al. Large energy storage density, low energy loss and highly stable $(\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_{0.66}\text{Sn}_{0.23}\text{Ti}_{0.11})\text{O}_3$ antiferroelectric thin-film capacitors[J]. *J Eur Ceram Soc*, 2018, 38(9): 3177–3181.
- [31] SHEN B Z, LI Y, HAO X H. Multifunctional all-inorganic flexible capacitor for energy storage and electrocaloric refrigeration over a broad temperature range based on PLZT 9/65/35 thick films[J]. *ACS Appl Mater Interfaces*, 2019, 11(37): 34117–34127.

Study on Energy Storage Performance of Flexible $\text{Pb}_{0.99}\text{Sm}_{0.01}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.68}\text{Ti}_{0.32}\text{O}_3$ Relaxor-Ferroelectric Film

LV Panpan¹, SHI Changqing¹, XIN Le³, ZHAN Hang¹, ZHANG Shuzhi¹, WANG Jia¹, LI Ruihang¹, LI Cuncheng¹, REN Luchao¹, YANG Changhong⁴, ZHANG Mingwei^{1,2}, CHENG Xin⁴

(1. School of Materials Science and Engineering, Shandong University of Technology, Zibo 255000, Shandong, China; 2. Analytical Texting Center, Shandong University of Technology, Zibo 255000, Shandong, China; 3. Department of Mathematics and Physics, Zibo Normal College, Zibo 255130, Shandong, China; 4. Shandong Provincial Key Laboratory of Preparation and Measurement of Building Materials, University of Jinan, Jinan 250022, Shandong, China)

Extended Abstract

Introduction Global energy crisis has sparked unprecedented momentum for renewable energy sources. Energy storage systems such as electrochemical capacitors, batteries, fuel cells, and dielectric capacitors are considered as the most important technologies to address rapidly growing energy demands and environmental concerns. In comparison with batteries or fuel cells, dielectric capacitors possess high power density resulting from their faster charging/discharging characteristics, which are advantageous for power electronics and pulse power applications. The majority of materials used for fabrication of dielectric capacitors consist of linear dielectrics, ferroelectrics, relaxor ferroelectrics, and anti-ferroelectrics. Among these materials, relaxor ferroelectrics are the most

popular choice for capacitor applications because of their lack of long-range order ferroelectric domains. $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $x\text{PbTiO}_3$ (PMNT) as the typical representative of relaxor ferroelectrics, which possesses small remanent polarization and low coercive electric field, enjoys promising prospects in dielectric capacitor application. Nevertheless, limited by its low E_b , the energy storage density and efficiency for pure PMNT film are not yet ideal. Moreover, it is difficult for traditional PMNT film to be bendable due to limitations of rigid substrates, which lead to descend of flexibility and cannot meet modern flexible electronic production requirements. In this paper, to overcoming the bottlenecks of inflexibility and inferior energy storage performance of the pure PMNT films, rare-earth element of Sm and promising LaNiO_3 (LNO) buffer layer were introduced into PMNT thin film. To obtain extraordinary flexibility, two-dimensional mica substrate was used to prepare the modified PMNT film via a simple sol-gel method. The microstructure, dielectric, ferroelectric and energy storage properties of the flexible $\text{Pb}_{0.99}\text{Sm}_{0.01}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.68}\text{Ti}_{0.32}\text{O}_3$ (PSMNT) film were studied systematically.

Methods The PSMNT and LNO films were prepared using a sol-gel method. First, niobium ethoxide ($\text{Nb}(\text{OC}_2\text{H}_5)_5$) was dissolved in 2-methoxyethanol at room temperature. And tetrabutyl titanate ($\text{Ti}(\text{OC}_4\text{H}_9)_4$) was stabilized in acetylacetone. Second, lead (II) acetate trihydrate ($\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$) with 10% excess Pb, samarium (III) nitrate hexahydrate ($\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), and magnesium (II) acetate tetrahydrate ($\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$) were dissolved together in a mixed solvent of glacial acetic acid and 2-methoxyethanol (volume ratio of 2:1) at room temperature. Then, the solutions above were mixed to obtain the PSMNT precursor. To prepare the LNO precursor, the lanthanum (III) nitrate hexahydrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) and nickel (II) acetate tetrahydrate ($\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$) were dissolved in 2-methoxyethanol. The concentration of the PSMNT and LNO precursors were $0.2 \text{ mol} \cdot \text{L}^{-1}$ and $0.1 \text{ mol} \cdot \text{L}^{-1}$, respectively.

The flexible mica substrate was separated from the bulk fluorophlogopite mica crystal by mechanical exfoliation using a razor blade in deionized water. When the thickness of the mica substrate was reduced to $\sim 15 \mu\text{m}$, good flexibility could be realized. The LNO precursor solution was firstly spin-coated onto the mica substrate, followed by an annealing process at 750°C for 2 min. Then, the PSMNT precursor was spin-coated on the surface of the freshly prepared LNO layer and then the wet film was annealed at 700°C . The spin-coating and annealing process was repeated to achieve a desirable film thickness. Finally, Au top electrodes, $\sim 200 \mu\text{m}$ in diameter, were sputtered on the film surface through a shadow mask for electrical properties measurements.

Results and discussion PSMNT and PMNT thin films were directly deposited on LaNiO_3 buffered mica substrate via simple one-step fabrication process. X-ray diffraction (XRD) results indicated that the crystal structure of PSMNT film was pure perovskite phase without detectable secondary phases. Scanning electron microscope (SEM) measurement revealed that the film exhibited compact microstructure with uniform crystal grain distribution, indicating that the PSMNT film can be successfully grown on the LaNiO_3 buffered mica substrate. In terms of polarization characteristics, slim hysteresis loop with a large maximum polarization P_{max} ($\sim 74.5 \mu\text{C}/\text{cm}^2$) and a small remnant polarization P_r ($\sim 16.4 \mu\text{C}/\text{cm}^2$) was observed in the PSMNT film under the electric field of $2.468 \text{ kV}/\text{cm}$, while fatted P - E loop was observed in the PMNT film. The leakage current density in the PSMNT film is almost an order of magnitude lower than the pure PMNT sample, indicating the success of the introduction of Sm in improving of electric resistance. The recoverable energy storage density for the PSMNT film capacitor at the maximum electric field was $40.7 \text{ J}/\text{cm}^3$, and the corresponding energy-storage efficiency was 70% due to its high breakdown strength and strong relaxor dispersion. The PSMNT film capacitor also exhibits excellent stability in energy storage performance in a wide operating frequency (1–20 kHz) and broad temperature (25 – 120°C) ranges. With the assistance of a mica substrate, the all-inorganic PSMNT/LNO/mica capacitor possesses an outstanding mechanical-bending resistance without obvious deterioration in its energy storage performance even down to a bending radius of 2 mm or repeated bending for 10^3 cycles.

Conclusions The main conclusions of this paper are summarized as following. Flexible $\text{Pb}_{0.99}\text{Sm}_{0.01}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.68}\text{Ti}_{0.32}\text{O}_3$ (PSMNT) film was successfully deposited on LaNiO_3 buffered mica substrate by a simple sol-gel method. A high recoverable energy density of $40.7 \text{ J}/\text{cm}^3$ and efficiency of 70% were realized in the fabricated film capacitor. The energy storage performance was quite stable in a wide temperature (25 – 120°C) and frequency (1–20 kHz) ranges. Meanwhile, the designed PSMNT film capacitor exhibited superior mechanical-bending resistance since it is attached on the bendable mica substrate, and its energy storage behavior did not show obvious deterioration even under a small bending radius of $R=2 \text{ mm}$ and 1 000 mechanical bending cycles ($R=4 \text{ mm}$). This study showed that flexible PSMNT thin film on mica platform has bright prospects in future flexible electronics application for energy storage.

Keywords lead magnesium niobate–lead titanate thin film; relaxor ferroelectrics; dielectric energy storage; flexibility