EFFECT OF OPERATING TEMPERATURE ON THE PERFORMANCE OF RELAXOR-FERROELECTRIC PLZT FILMS-BASED POWER ENERGY-STORAGE DEVICES

Dang Thi Ha, Nguyen Vu Cam Binh, Bui Thi Toan Thu, Nguyen Thi Luc, Le Thai Ha
Vietnam National University of Forestry

https://doi.org/10.55250/jo.vnuf.2023.15.158-164

ABSTRACT

Thermal stability is a key factor to determine the applicability of dielectric capacitors in the power energy-storage devices. The effects of operating temperature on the polarization hysteresis, energy-storage performance, and charge-discharge cycling stability of thin-film capacitors have been revealed in this study by investigating the relaxor $Pb_{0.92}La_{0.08}(Zr_{0.52}Ti_{0.48})O_3$ (PLZT) thin film grown on $Pt/Ti/SiO_2/Si$ substrates using a sol-gel spin-coating technique. The PLZT thin films demonstrate good thermal stability of polarization hysteresis and outstanding energy storage properties over a wide temperature range from room temperature to 150°C. With increasing operating temperature up to 200°C, the polarization hysteresis loops gradually become more slanted and slightly broaden. The fluctuation in recoverable energy density is less than 8%, and the change of energy-storage efficiency is less than 12% at 200°C, which may be associated with the high dynamic polar nanoregions (PNRs) in relaxor ferroelectrics. At room temperature, PLZT thin film shows an excellent charge-discharge cycling life with fatigue-free performance after 10^{10} cycles in both discharge energy-storage density and energy-storage efficiency. However, the reduction of discharge energy-storage density and energy-storage efficiency, performed at an operating temperature of 200°C, is about 18% after 10^{10} charge-discharge cycles. All these results suggest that such PLZT thin film capacitors are very attractive for energy-storage applications operating under high-temperature conditions.

Keywords: Charge-discharge endurance, energy storage system, relaxor ferroelectrics, sol-gel, thin film.

1. INTRODUCTION

With the fast development of the power electronics, dielectric materials with high energy-storage density, low loss, and good temperature stability are eagerly desired for the potential application in advanced pulsed capacitors. Based on the physical principles, the materials with higher saturated polarization, smaller remnant polarization, and higher electrical breakdown field are attracted increasing attention. Relaxor ferroelectrics (RFE) were predicted to be promising candidates for high energy storage application because it has rather large saturated polarization, small remnant polarization, moderate breakdown field and high energy storage density [1]. For example, it was reported that the energy storage density is 22 J/cm^3, energy storage e ciency of ~77% at dielectric breakdown strength of ~ 1600 kV/cm in PLZT (9/52/48) thin lms deposited on LNO bu ered nickel substrates [2]. N Ortega et al. [3] reported a high energy storage capability of 46 J/cm^3 with a very high breakdown eld of 5000 kV/cm in (BT/BST) thin films. Another result, a large recoverable energy-storage density of 28.7 J/cm^3 was obtained in the thin lms at 1000 Hz and a higher critical breakdown eld of 2177 kV/cm at room temperature in PLZT (9/65/35) thin films [4]. Among these result, the high energy density (46 J/cm^3) only can be achieved at room temperature due to lower breakdown voltage at higher temperature and by far, the vast majority of investigations on PLZT-based ferroelectric thin lms are focused on the energy storage properties at room temperature. In practical applications, the device operation temperature may uctuate within a certain range. For example, the working temperature is up to ≈140°C for power electrics in hybrid electric vehicles [5]. Therefore a competent energy storage material requires not only a high energy density but also high thermal stability.

This makes the thermal stability of the energy storage capacitors an important parameter and has prompted some interesting studies recently [6]. $Pb_{0.8}Ba_{0.2}ZrO_3$ (PBZ) relaxor thin lms, which were prepared on a $Pt/TiO_x/SiO_2/Si(100)$ substrate by using a sol-gel method, exhibits the variation of the temperature-dependent energy density of within 5% from room temperature to 150°C [7]. These values are very stable from room temperature to 150ºC [2]. The recoverable energy density was found almost temperature independent in the tested temperature range from room temperature to 180°C in $Pb_{0.92}La_{0.08}Zr_{0.52}Ti_{0.48}O_3$ (PLZT) thin lm that were fabricated using pulsed laser deposition on (001) Nb-doped $SrTiO_3$ (Nb:STO) substrates [6]. However, to the best of our knowledge, a large energy storage density with simultaneous high thermal stability in $Pb_{0.92}La_{0.08}Zr_{0.52}Ti_{0.48}O_3$ (PLZT) thin lms which were fabricated on a $Pt/Ti/SiO_2/Si(100)$ substrate by using a sol gel method is rarely reported. In this study, the highly pseudocubic (100)-oriented $Pb_{0.92}La_{0.08}Zr_{0.52}Ti_{0.48}O_3$ relaxor thin lm were prepared by sol-gel processing. The effect of temperature on the ferroelectric properties is investigated, and the superior charge-discharge endurance for long-term stability is also studied. At room temperature, PLZT thin film showed an excellent charge-discharge energy performance up to 10^{10} cycles. Gradually increasing operating temperature to 200°C, the polarization hysteresis loops become slanted and slightly broaden. At temperature of 200°C and after 10^{10} cycles, recoverable energy and energy-storage efficiency displayed a slightly reduction of 12% and 18%, respectively.

2. EXPERIMENTAL PROCEDURE

2.1. Sol-gel spin-coating process

The $Pb_{0.92}La_{0.08}(Zr_{0.52}Ti_{0.48})O_3$ thin films were prepared using a sol-gel spin-coating process [8]. Lead acetate trihydrate ($Pb[CH_3COO]_2.3H_2O$), lanthanum nitrate ($La[NO_3]_3$), titanium iso-propoxide ($Ti[i\text{-}OPr]_4$) and zirconium n-propoxide ($Zr[n\text{-}OPr]_4$) were used as the starting materials. In this process, 2-methoxy ethanol (MOE) was used as a solvent, while acetic acid was used as the function of a catalyzer. In order to compensate for the lead loss during annealing/sintering and to prevent the formation of a pyrochlore phase in the films, 15 mol% excess lead was added into the starting solution. Lead acetate and lanthanum nitrate were dissolved in MOE on heating at 90°C with an acetic acid catalyst and then refluxed at 124°C for 10h. Titanium iso-propoxide and MOE were refluxed at 124ºC for 5h, while zirconium n-propoxide and MOE were refluxed at 124°C for 4h. After that, the complex solution was stirred well at 124°C for 3h to obtain a homogeneous solution. The 0.4 M PLZT precursor solutions were then deposited onto $(111)Pt/Ti/SiO_2/Si$ (Pt/Si) substrates by spin-coating at 2000 rpm for 30s, followed by pyrolysis at 400°C for 10 min. This process was repeated for 5 times. Finally, the films were then annealed at 650°C for 60 min in air. The final thickness of the films was ~250 nm.

2.2. Measurement process

Crystallographic properties of the thin film were analyzed by X-ray θ-2θ scans (XRD) using a PANalytical *X-ray* diffractometer (MalvernPANalytical) with Cu-Kαradiation (wavelength: 1.5405 Å). Normal operating power is 1.8 kW (45 kV and 40 mA). Atomic force microscopy (AFM: Bruker Dimension Icon) and cross-sectional high-resolution scanning electron microscopy (HRSEM, Zeiss-1550, Carl Zeiss Microscopy GmbH) were performed to investigate the morphology, microstructure, and thickness of the as-grown thin film.

For the electrical measurements, the Pt electrode pads of (200×200 μm^2 in size) were

made on top of the PLZT lms by dc sputtering. The polarization-electric field (*P-E*) hysteresis loops were measured with the dynamic hysteresis measurement (DHM) option of the ferroelectric module of the aixACCT TF-2000 Analyzer (aixACCT Systems GmbH). The ferroelectric charge-discharge cycling fatigue measurements were performed with a bipolar switching pulse of 200 kV/cm and a pulse height at a 100 kHz repetition frequency. A Keithley 4200 semiconductor characterization system (Tektronix, Beaverton-Oregon, United States) was used for the leakage current measurements.

The energy-storage density, U_{store}, the recoverble energy storage density, U_{reco} and the energy storage efficiency, η of a dielectric capacitor are calculated from the polarization hysteresis loop as indicated in Figure 1 according to the equations (1)-(4) as follows.

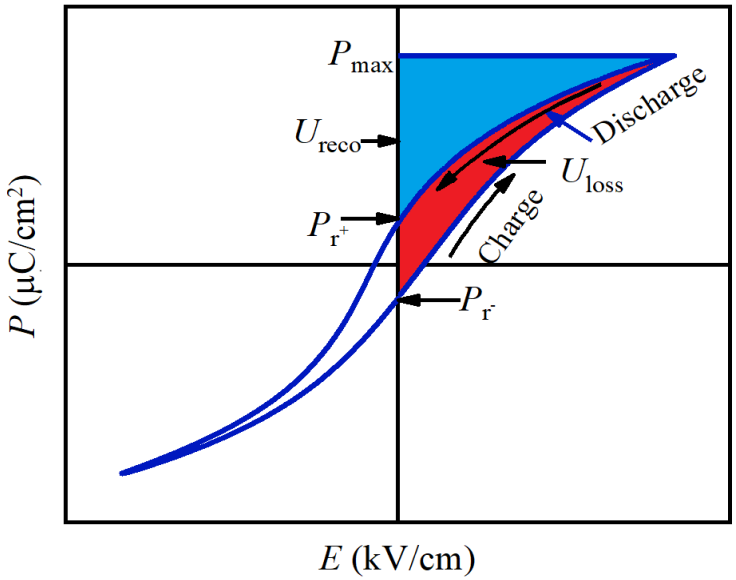

Figure 1. Schematic of electric-field-induced polarization hysteresis (P-E) loop of an relaxor ferroelectric material.

$$U_{store} = \int_{P_{r-}}^{P_{max}} EdP \quad (1)$$

$$U_{reco} = \int_{P_{r+}}^{P_{max}} EdP \quad (2)$$

$$U_{loss} = U_{store} \quad U_{reco} \quad (3)$$

$$\eta(\%) = 100 \times U_{reco}/U_{store} \quad (4)$$

where E is the electric eld, and P is the polarization. When the electric eld increases from zero to the maximum (E_{max}), the polarization increases to the maximum (P_{max}), and electric energy is stored in the capacitor as (U_{store}). The recoverable electric energy density (U_{reco}) is then released on discharge from (E_{max}) to zero, represented by the blue area in Figure 1.

3. RESULTS AND DISCUSSION

3.1. Structure

Figure 2a shows X-ray diffraction (XRD) patterns taken at room temperature from PLZT lms annealed at 650°C. Only the perovskite phase of PLZT was obtained, which had a strong preferred pseudocubic (100) orientation. Other peaks were measurable from this lms with minor (110) and (111) orientations. The surface morphology AFM and the cross-sectional SEM image of PLZT (8/52/48) are shown in Figure. 2(b, c). AFM topographic scans show that the root-mean-square roughness of the PLZT thin film is about 4.2-4.6 nm. The cross-sectional SEM image shows that the PLZT lms are dense, uniform, and crack-free. No impurities such as pyrochlore/ uorite phases were observed in the

XRD pattern and SEM image. The thickness of the PLZT (8/52/48) lm with five layers of coating is about 250 nm, as determined by cross-sectional SEM, resulting in a per-coating thickness of 50 nm.

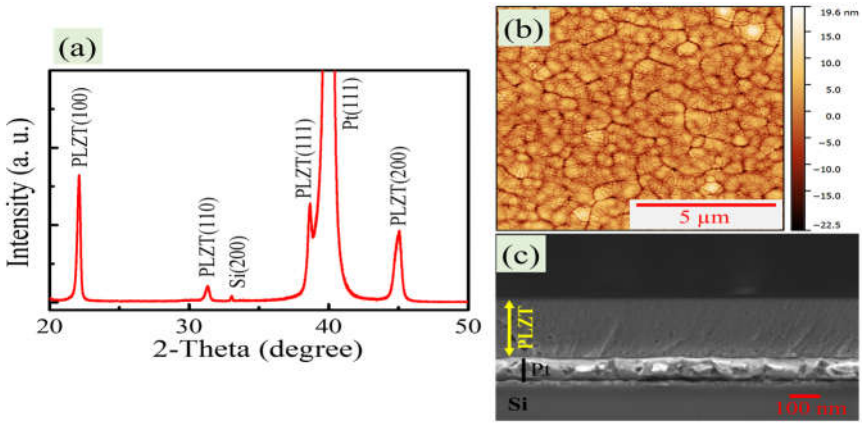

Figure 2. (a) XRD, (b) AFM and (c) cross-sectional SEM, of the 8% La-doped PLZT thin film.

3.2. Energy Storage

Fatigue of ferroelectric materials refers to the reduction of switchable polarization after repetitive electrical cycling. It is detrimental to the performance and lifetime of ferroelectric-based devices, such as ferroelectric random access memory (Fe-RAM), actuators, and microwave electronic components [9]. From a practical application point of view, superior charge-discharge endurance for long-term stability is also very important for energy-storage devices. Figure 3 gives the electrical polarization fatigue behavior of the PLZT thin films on Pt/Si substrates as a function of the number of switching cycles up to 10^{10} cycles. The fatigue testing was performed at room temperature (25°C). Figure 3(a) shows that both (P_r) and (P_{max}) values increase with the number of bipolar fatigue cycles. The charge-discharge cycling affects very little on the (*P-E*) loops before and after 10^{10} fatigue cycles. As seen in Figure 3(b) that the (*P-E*) loops varied slightly with cycling.

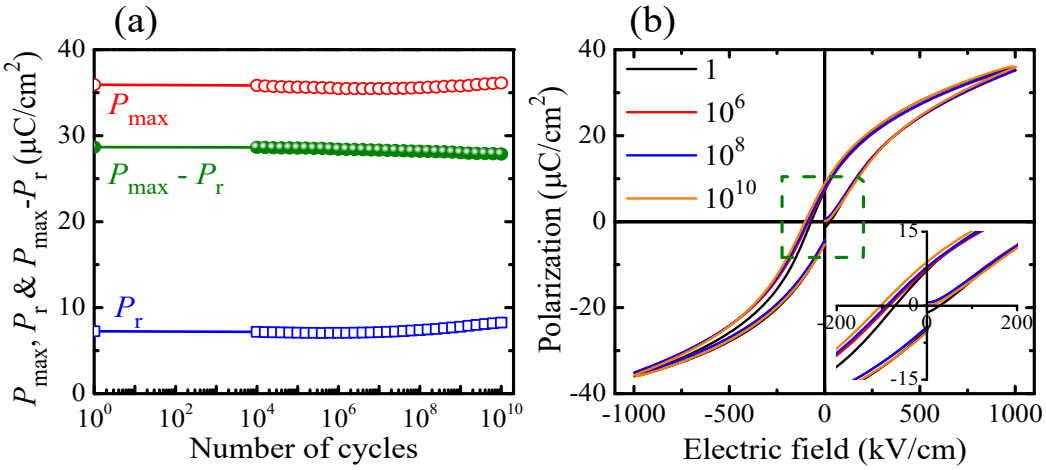

Figure 3. (a) P_{max} and P_r values as a function of number charge-discharge cycles and (b) comparison of P-E hysteresis loops measured at different charge-discharge cycles under an applied electric field of 1000 kV/cm and 1 kHz, of the 8% La-doped PLZT thin film. The fatigue testing was performed by applying a bipolar electric field of pulse height 200 kV/cm, pulse width 100 kHz (or 5 μs) and at room temperature

Figure 4 show the plots of U_{store}, U_{reco}, and η data against the number of charge-discharge cycles obtained from the *P-E* loops of the PLZT thin film, measured at 1 kHz and room temperature. It was found that U_{reco} reduced slightly while U_{store} increased. Consequently, η

value reduced slightly about 2 - 2.5%. This result implies good charge-discharge cycles stability of the energy-storage performance at room temperature.

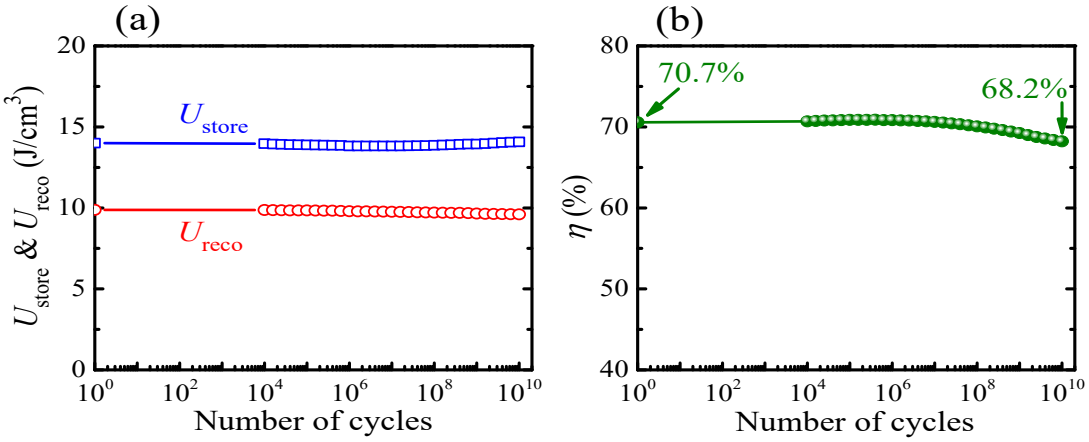

Figure 4. Dependence of (a) energy storage density (U_{store} and U_{reco}) and (b) energy storage efficiency (η) on cycling for the 8% La-doped PLZT thin film. The data were calculated from the corresponding *P-E* hysteresis loops performed at 1000 kV/cm, 1 kHz and at room temperature.

An important FOM for energy-storage device is the energy storage efficiency (η). In addition, the thermal stability of the energy storage performance should also be considered for real capacitor applications. To investigate the temperature-dependent stability of the PLZT thin film, the energy-storage density and the energy-storage efficiency were measured at 1 kHz in the temperature range from 25 to 200°C. These obtained data are presented in Figure 5.

Upon increasing operating temperature, from room temperature to 200°C, the polarization hysteresis loops gradually become more slanted and slightly broadened (Figure 5a). This trend can be explained by the thermal activation energy theory of the domain wall movement. The higher thermal energy at an increased temperature facilitates the ferroelectric domain movement and hence increases the remnant polarizations [6].

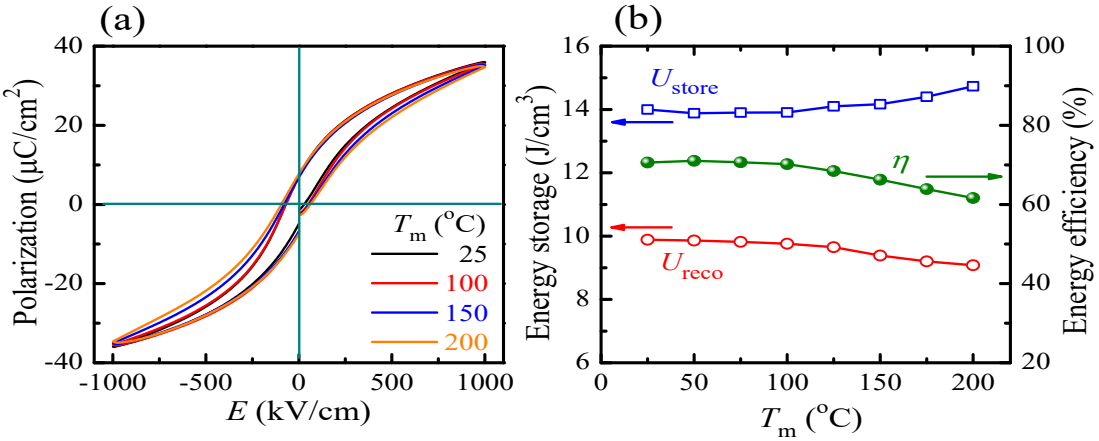

Figure 5. Operating temperature dependence (T_m) of (a) P-E loops, (b) energy-storage density (U_{store} & U_{reco}) and energy-storage efficiency (η), for the 8% La-doped PLZT thin film. The measurements were performed at 1 kHz.

Similar to the trend of U_{reco}, the energy storage e ciency, η decreases with an increase of the temperature and approximately 47.1% at 200°C. The fluctuation in discharge energy-storage density is about 8%, and the change of energy-storage efficiency is around 12% (Figure 5b), which may be associated with the high dynamic polar nanoregions (PNRs) in relaxor ferroelectrics. It can be explained by considering the asymmetric distribution of

polar nano regions.

Figure 6 displays the electrical polarization fatigue behavior of the PLZT thin films on Pt/Si substrates as a function of the number of switching cycles up to 10^{10} cycles. The fatigue testing was performed at 200°C. Figure 6(a) shows that both P_r and P_{max} values increase with the number of bipolar fatigue cycles, in which P_r increases more than P_{max}. The charge-discharge cycling significantly affects the (*P-E*) loops before and after 10^{10} fatigue cycles. As observed in Figure 6(b), the (*P-E*) loops shifts slightly to the negative electric field side.

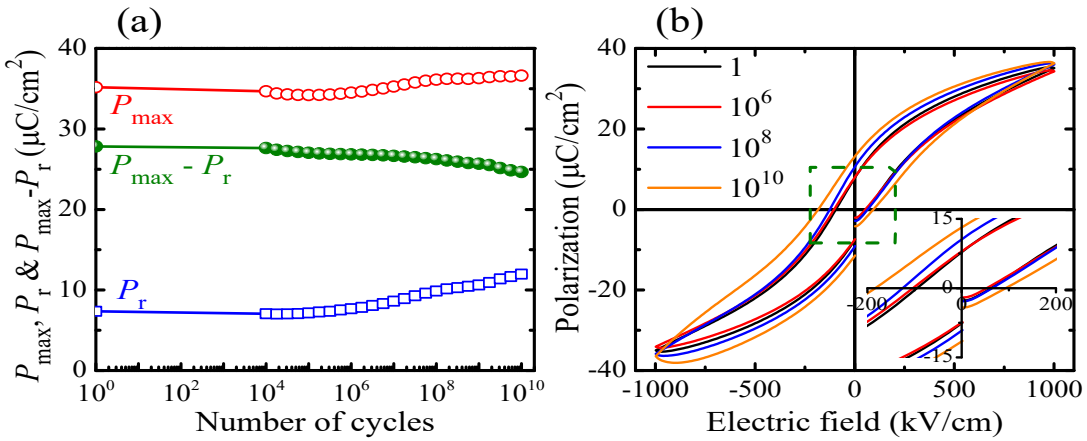

Figure 6. (a) P_{max} and P_r values as a function of number charge-discharge cycles and (b) comparison of *P-E* hysteresis loops measured at different charge-discharge cycles under an applied electric field of 1000 kV/cm and 1 kHz, of the 8% La-doped PLZT thin film. The fatigue testing was performed by applying a bipolar electric field of pulse height 200 kV/cm, pulse width 100 kHz (or 5 μs) and at 200 ºC.

Figure 7 show the plots of U_{store}, U_{reco}, and η values against the number of charge-discharge cycles obtained from the (*P-E*) loops measurements of the PLZT thin film at 1000 kV/cm, 1 kHz at 200°C. Compared to the measured U_{reco} value at room temperature, the measured U_{reco} value at 200°C decreased significantly, and η value is reduced about 18%. These results suggest that the discharge cycle of the PLZT thin film has a significant impact on the energy-storage performance at high temperatures.

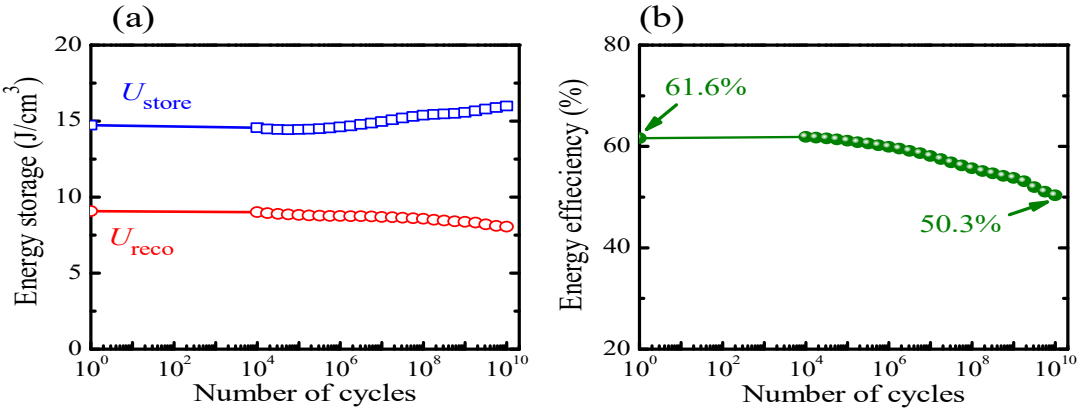

Figure 7. Dependence of (a) energy storage density (U_{store} and U_{reco}) and (b) energy storage efficiency (η) on cycling for the 8% La-doped PLZT thin film. The data were calculated from the corresponding (*P-E*) hysteresis loops performed at 1000 kV/cm, 1 kHz and at 200°C.

4. CONCLUSIONS

$Pb_{0.92}La_{0.08}(Zr_{0.52}Ti_{0.48})O_3$ (PLZT) thin lms were successfully deposited onto Pt/Si substrate using a spin-coated sol-gel method. The effects of operating temperature on the energy-storage performance, and charge-discharge cycling stability of the PLZT thin film have been investigated in detail. The results indicated that our 250 nm thick PLZT/Pt/Si thin film possesses the following

attractive properties for energy storage applications: PLZT thin film exhibited strong charge-discharge fatigue endurance up to 10^{10} cycles at room temperature. Despite the even lower values of U_{reco} (-12%) and η (-18%) obtained in the PLZT at temperature of 200°C and after 10^{10} cycles, PLZT thin film capacitors still can be a promising candidates for high-temperature energy storage capacitor applications.

Acknowledgments

The authors would like to acknowledge the financial support from the Foundation for Science and Technology Development of Vietnam National University of Forestry.

REFERENCES

[1]. Hao X. (2013). A review on the dielectric materials for high energy-storage application. Journal of Advanced Dielectrics. 3(01): 1330001.

[2]. Tong S., Ma B., Narayanan M., Liu S., Koritala R., Balachandran U. & Shi D. (2013). Lead lanthanum zirconate titanate ceramic thin films for energy storage. ACS applied materials interfaces. 5(4): 1474-1480.

[3]. Ortega N., Kumar A., Scott J., Chrisey D. B., Tomazawa M., Kumari S., Diestra D. & Katiyar R. (2012). Relaxor-ferroelectric superlattices: high energy density capacitors. Journal of Physics: Condensed Matter. 24(44): 445901.

[4]. Hao X., Wang Y., Yang J., An S. & Xu J. (2012). High energy-storage performance in $Pb_{0.91}La_{0.09}(Ti_{0.65}Zr_{0.35})O_3$ relaxor ferroelectric thin films. Journal of applied physics. 112(11): 114111.

[5]. Johnson R. W., Evans J. L., Jacobsen P., Thompson J. R. & Christopher MJItoepm (2004). The changing automotive environment: high-temperature electronics. 27(3): 164-176.

[6]. Hu G., Ma C., Wei W., Sun Z., Lu L., Mi S.-B., Liu M., Ma B., Wu J. & Jia C-l (2016). Enhanced energy density with a wide thermal stability in epitaxial $Pb_{0.92}La_{0.08}Zr_{0.52}Ti_{0.48}O_3$ thin films. Applied Physics Letters. 109(19): 193904.

[7]. Peng B., Zhang Q., Li X., Sun T., Fan H., Ke S., Ye M., Wang Y., Lu W. & Niu H. (2015). Large energy storage density and high thermal stability in a highly textured (111)-oriented $Pb_{0.8}Ba_{0.2}ZrO_3$ relaxor thin film with the coexistence of antiferroelectric and ferroelectric phases. ACS applied materials interfaces. 7(24): 13512-13517.

[8]. Dang Thi Ha, Trinh Thi Trang, Nguyen Thi Quynh Chi, Do Van Truong, Nguyen Duc Minh & Vu Ngoc Hung (2019). Enhancement of relaxor behavior by La doping and its influence on the energy storage performance and electric breakdown strength of ferroelectric $Pb(Zr_{0.52}Ti_{0.48})O_3$ thin films. Materials Chemistry. 234: 210-216.

[9]. Zou X., You L., Chen W., Ding H., Wu D., Wu T., Chen L. & Wang J. (2012). Mechanism of polarization fatigue in $BiFeO_3$. Acs Nano. 6(10): 8997-9004.

ẢNH HƯỞNG CỦA NHIỆT ĐỘ ĐẾN HIỆU SUẤT CHUYỂN ĐỔI CỦA CÁC THIẾT BỊ TÍCH TRỮ NĂNG LƯỢNG DỰA TRÊN CƠ SỞ MÀNG MỎNG SẮT ĐIỆN NHÒE PLZT

Đặng Thị Hà, Nguyễn Vũ Cẩm Bình, Bùi Toàn Thư, Nguyễn Thị Lục, Lê Thái Hà

Trường Đại học Lâm nghiệp

TÓM TẮT

Độ ổn định nhiệt khi làm việc là yếu tố quan trọng quyết định đến khả năng ứng dụng của các thiết bị tích trữ năng lượng. Nghiên cứu này đã khảo sát ảnh hưởng của nhiệt độ và số chu kỳ sạc/xả đến tính chất sắt điện, hiệu suất tích trữ năng lượng của tụ sắt điện màng mỏng $Pb_{0.92}La_{0.08}(Zr_{0.52}Ti_{0.48})O_3$ (PLZT) quay phủ trên đế $Pt/Ti/SiO_2$ bằng kỹ thuật sol-gel. Các màng mỏng PLZT thể hiện tính ổn định nhiệt về đặc tính trễ phân cực điện và đặc tính tích trữ năng lượng trong dải nhiệt độ rộng từ nhiệt độ phòng đến 150°C. Với nhiệt độ khảo sát lên đến 200°C, các đường cong điện trễ nghiêng và hơi rộng hơn. Mật độ tích trữ năng lượng giảm 8%, hiệu suất tích trữ giảm 12% ở 200°C, có thể liên quan đến các vùng nano phân cực (PNR) trong vật liệu sắt điện nhòe. Ở nhiệt độ phòng, tính mỏi của vật liệu màng mỏng PLZT hầu như không suy giảm sau 10^{10} chu kỳ sạc/xả, mật độ và hiệu suất tích trữ năng lượng gần như không thay đổi. Tuy nhiên, khi khảo sát ở 200°C tính mỏi của vật liệu màng mỏng PLZT có suy giảm đôi chút sau 10^{10} chu kỳ. Mặc dù mật độ năng lượng phục hồi giảm 12%, hiệu suất chuyển đổi năng lượng giảm 18% ở điều kiện nhiệt độ 200°C và sau 10^{10} chu kỳ sạc/xả, PLZT vẫn có thể là vật liệu tiềm năng cho các ứng dụng tích trữ năng lượng trong điều kiện nhiệt độ cao.

Từ khóa: Vật liệu sắt điện nhòe, màng mỏng, sol-gel, độ bền sạc/xả, hệ thống tích trữ năng lượng.

Received : 25/11/2022
Revised : 30/12/2022
Accepted : 16/01/2023