Extended Abstracts of the 2014 International Conference on Solid State Devices and Materials, Tsukuba, 2014, pp206-207

(001) orientation single crystalline PZT pyroelectric nanorod array synthesized by hydrothermal reaction

C.G. Wu, Q.X. Peng, X. Y. Sun, J. Meng, Y. Shuai, J.Q. Cao, W.B.Luo, W. L. Zhang

State Key Lab of Electronic Thin films and Integrated Devices, University of Electronic Science and Technology of China, Chengdu 610054, China
Phone: +86-28-83202140 E-mail: cgwu@uestc.edu.cn

Abstract

The fabrication and pyroelectric coefficient of PZT nanorod array on NSTO substrates were reported. XRD and TEM revealed that PZT nanorods were (001) orientation single crystalline. Dense PZT nanorod array were synthesized on NSTO using optimal 0.8 g L^{-1} PVA and 3.2 g L^{-1} PAA. Maximum pyroelectric coefficient, 5.8×10^{-9}C/cm^{2}K, was measured for samples synthesized at 230°C and poled under 5V. The single crystalline PZT nanorod array material has potential application in small spatial (1-10 μ m) infrared detectors, benefiting to achieve distinguished detector performances.

1. Introduction

Nanorod materials have attracted many research interesting because of its size confinement only in radial direction while free scale along the length direction and its potential application in electric nanodevice [1]. Perovskite oxide materials, such as $BaTiO_3$, $KNbO_3$, $Pb(Zr_xTi_{1-x})O_3$, are widely studied due to excellent ferroelectric properties and potential application in nanodevice [2-4]. Whereas, the pyroelectric properties of the single crystalline PZT nanorod array on $Nb:SrTiO_3$ (NSTO) was not reported by now.

In this paper, single crystalline PZT nanorod was synthesized through optimizing surfactants amount of polyvinylalcohol (PVA) and polyacrylate acid (PAA). PZT nanorod array perpendicular to the NSTO substrate were obtained and the pyroelectric coefficient was given.

2. Experiments

Firstly, Lead nitrate ($Pb(NO_3)_2$) and zirconium nitrate pentahydrate ($Zr(NO_3)_4 \cdot 5H_2O$) were dissolved in 60 mL deionized water and magnetic stirred until colorless and transparent precursor solution was obtained. Secondly, the pre-prepared tetrabutyltitanate ($(C_4H_9O)_4Ti$) with 2 mL ethanol was gradually dropped into the above solution and mixed homogeneously by stirring for 30 min. The atomic ratio of Pb:Zr:Ti was 10:3:7 and the final Pb^{2+} Concentration was 0.1 M L^{-1}. Thirdly, PAA (MW = 900) and PVA were orderly dropped into the solution. Finally, 1.5 M L^{-1} alkali KOH was added when the solution was stirred quickly. After stirring for 30 min, the solution was transferred to 100 mL Teflon-lined stainless steel autoclave, NSTO substrate was horizontally hanged in the solution to grow PZT nanorod array. Hydrothermal reaction was performed at 175-230°C for 12 h in furnace.

Phase composition and structure were performed using powder X-ray diffraction (XRD, DX-1000, Dandong) analysis. The size and morphology of the synthesized PZT nanorod were determined by field-emission scanning electron microscopy (SEM, Inspect F, Holland). Transmission electron microscopy (TEM, JEM2012-HT) was used to investigate the microstructure of the PZT nanopowder and nanorod.

200nm Pt/100nm Ti was sputtered on the PZT surface to be as top electrode. Pyroelectric coefficient was measured by dynamic method.

3. Results and Discussion

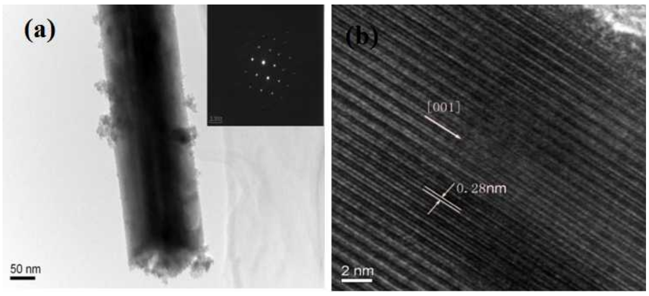

Fig.1 TEM images of PZT nanorod (a) single nanorod, inset SAED pattern, (b) HRTEM.

It could be observed from Fig. 1a that the nanorod had cuboid morphology and the size in radial direction was about 180 nm. The single crystalline state of a typical nanorod was revealed by the diffraction dots in the inset SAED in Fig. 1a. Fig.1b reveals that the nanorods were (001) orientation with lattice parameter a=0.28nm.

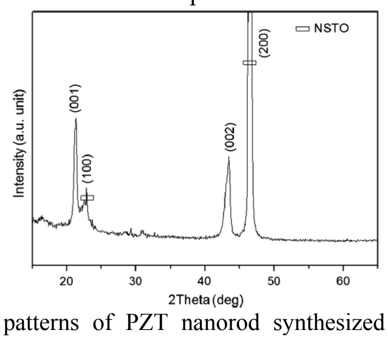

Fig.2 XRD patterns of PZT nanorod synthesized on Nb-STO substrates.

Fig.2 showed the XRD patterns of the PZT nanorods on NSTO. It revealed the (001) orientation of the PZT array, which is consist with that of TEM. The strong peaks of the (100)-NSTO originated from where the area was coated with short PZT rod or none.

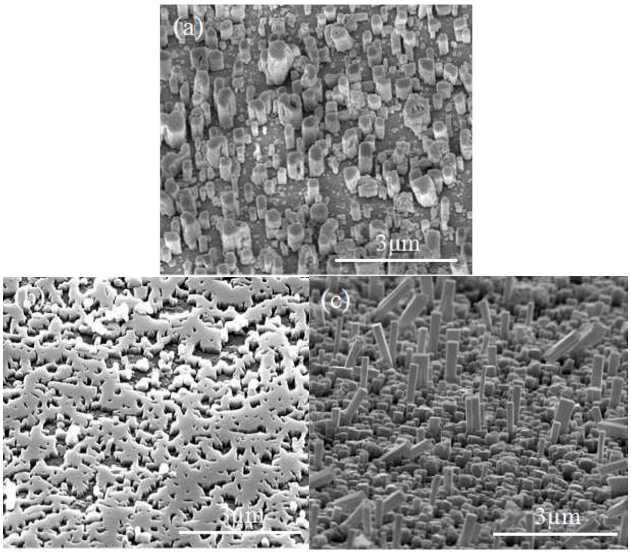

Fig.2 SEM images of PZT nanorod array synthesized at (a) 175°C, (b) 210°C, (c) 230°C.

The PZT nanorod array grown on NSTO was conducted with 0.8 g L^{-1} PVA and 3.2 g L^{-1} PAA. Fig.2 is the SEM morphology of the PZT nanorod array synthesized at various temperatures with 30° tilt view. It could be seen that dense PZT nanorods grew nearly vertically to the substrate, which was attributed to the surface energy difference caused by absorption of PVA and PAA on different crystal plane [5]. The radial size was less than 200 nm although cohesive rods were found which were labeled in black box. The length difference of the major rods was very little and a small number of rods were extremely long. The bad uniformity of length might be caused by the composition fluctuation of hydrothermal solution.

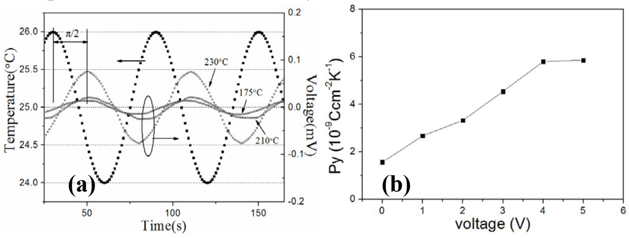

Fig.3 pyroelectric coefficient measurement data of PZT nanorod array (a) synthesized at 175°C, 210°C and 230°C, (b) poled under 0-5 DC voltages.

1×1 mm^2 capacitance structure was formed with NSTO bottom electrode, PZT nanorods dielectric material and Pt up electrode. The pyroelectric coefficients of the PZT nanorods before and after poling were tested by dynamic method and the voltage responses were showed in Fig. 3.

Pyroelectric coefficient of virgin samples synthesized at 175°C, 210°C and 230°C was 5×10^{-10}, 9×10^{-10}, and 1.5×10^{-9}C/cm^2K, respectively. The results were shown in Fig. 3a. For sample fabricated at 230°C, ferroelectric poling were performed under 1-5 DC voltages at 150°C for 15 minutes. Fig. 3b gave the measurement data. It can be seen that pyroelectric coefficient increase linearly with increasing poling voltage, and was saturation to 5.8×10^{-9}C/cm^2K when poling voltage was larger than 4V.

4. Conclusions

Single crystalline PZT nanorods of cuboid morphology were successful obtained in hydrothermal reaction by adding PVA and PAA. The orientation growth of PZT nanorod was attributed to the surface energy difference caused by absorption of PVA and PAA on different crystal plane.

HRTEM image and SAED pattern show the PZT nanorods were (001) orientation single crystalline. Dense PZT nanorods were synthesized on NSTO at temperature 175-230°C. Maximum pyroelectric coefficient, 5.8×10^{-9}C/cm^2K, was measured for samples synthesized at 230°C and poled under 5V. In next work, small spatial (1-10μm) infrared detectors utilizing PZT nanorod array material will be developed. Attributing to very low thermal capacitance and perfect single crystalline of PZT nanorod material, the infrared detectors would have distinguished performances.

References

[1] Y. Yang, Y.S. Zhou, J.M. Wu, Z.L. Wang, ACS Nano, 2012, 6(9), 8456-8459.
[2] B. Im, H. Jun, K.H. Lee, S.H. Lee, I.K. Yang, Y.H. Jeong, J.S.Lee, Chem. Mater., 2010, 22(16), 4806-4810.
[3] A. Magrez, E. Vasco, J.W. Seo, C. Dieker, N. Setter, L. Forro, J. Phys. Chem. B, 110(1), 2006, 58-62.
[4] Q. X. Peng, C.G. Wu, W.B. Luo, C. Chen, G.Q. Cai, X.Y. Sun, Infrared Physics & Technology, 2013, 61, 313－318.
[5] Y. Yoshida, M. Tochimoto, D. Schlettwein, D. Wohrle, T. Sugiura, H. Minoura, Chem. Mater., 1999, 11, 2657-2662.