

Ferroelectric single-crystal nano-rods grown within a nano-porous aluminum oxide matrix

Doron Yadlovker · Shlomo Berger

Received: 19 February 2007 / Accepted: 9 November 2007 / Published online: 6 March 2008
© Springer Science + Business Media, LLC 2007

Abstract Growing ferroelectric nano single-crystals with uniform polar direction in-vertical to the substrate plane is of high scientific and technological interest for understanding ferroelectric behavior in small dimensions and developing future devices. Single-crystals of Rochelle Salt (RS) and potassium nitrate (PN), with preferred orientation, were grown inside a highly-dense array of aluminum oxide nano-pores, oriented in-vertical to the substrate plane. Preferred orientation was also obtained for potassium niobate crystals. Under certain conditions, nucleation occurred only at the pore bottom due to a tight control over temperature, liquid composition, and pore size. Nucleation at the bottom is necessary for the formation of identically-aligned single-crystals within the pores. Non-linear dielectric behavior was observed in the case of RS and PN crystals inside the pore. The pores stabilize the ferroelectric phase of RS up to 30°C above the upper Curie temperature of bulk (24°C). In the case of PN-filled pores, the crystals grow in the non-ferroelectric orthorhombic phase. Upon applying an electric field of 200 kV/cm, a transition to the ferroelectric phase occurs, and a hysteresis loop appears. This phenomenon was not observed in bulk PN and is attributed to the effect of the hydrostatic pressure applied by the pore walls combined with the applied electric field.

Keywords Porous aluminum oxide film · Single-crystal nano-rods · Uniform crystallographic orientation · Thin composite films

D. Yadlovker · S. Berger (✉)
Faculty of Materials Science and Engineering, Technion,
Haifa 32000, Israel
e-mail: berger@tx.technion.ac.il

1 Introduction

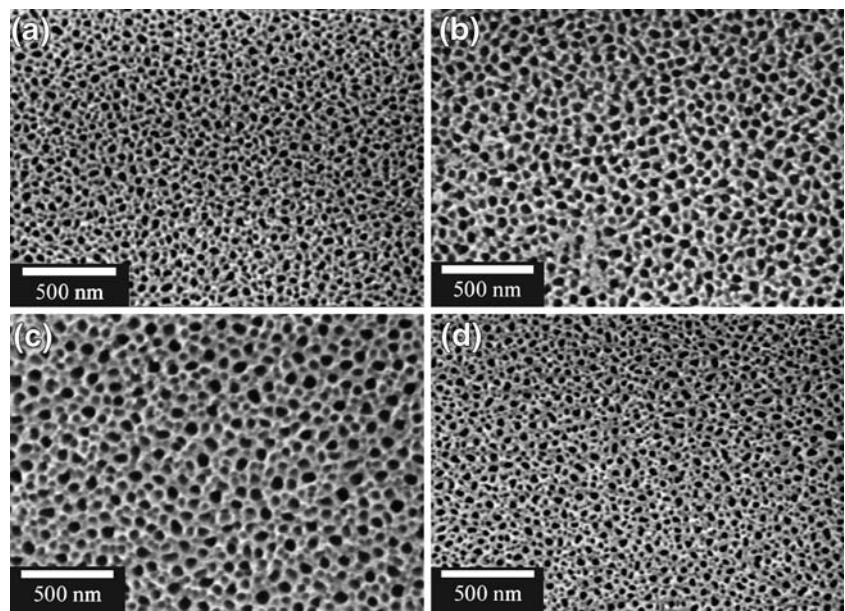
The subject of template-based growth of ferroelectrics has gained much attention in recent years [1–5] motivated by the search for understanding the effect of small particle size and the high-density of interfaces on the physical properties of the ferroelectric material. The study of this subject is also interesting for industrial applications such as high-density and high-resolution devices, where each nano-single-crystal may serve as a sensor, detector, actuator or memory-cell. A major challenge is controlling the size, alignment and crystallographic orientation of the nano-particles within the template, in order to obtain a homogeneous response. One way of confronting this challenge is using tubular templates, which can be made of a polymer, a ceramic [1, 3], or a semiconductor material [2, 3]. In all cases a poly-crystalline phase was grown inside the templates with no preferred crystallographic orientation.

In this paper we present the ability to grow single crystal nano-rods inside aluminum oxide tubular nano-pores. The crystals have preferred crystallographic orientation and in some cases unique dielectric behavior.

2 Experimental

The fabrication process of the pores consists of electro-chemical anodization of aluminum substrate in an aqueous solution of phosphoric acid (3 vol.%) under conditions of either constant current density or constant voltage at 25°C. The anodized samples were immersed in an aqueous solution of RS, PN or potassium niobate. All solutions were prepared by dissolving pure powder in deionized water. The pores were filled, aided by capillary forces [6].

Fig. 1 Anodized aluminum oxide (AAO) templates with different pore sizes obtained under: (a) 20 V, (b) 30 V, (c) 50 V, and (d) 1.6 mA



The aqueous solutions were slowly cooled, and crystals grew inside the pores from the saturated solution. The effect of different parameters such as saturation temperature and cooling rate of the liquid solution on the crystallographic orientation of the crystals was examined. In the case of RS, the saturation temperature was about 40°C. For PN, two solutions with saturation temperatures of 40 and 70°C were used, and in the case of potassium niobate, which is almost insoluble in water, the solution was constantly saturated, and the pores were immersed in the solution at two different temperatures of 37 and 44°C. Crystal growth occurred during a slow cooling (about 0.25°C/min) of the liquid solution to about room temperature. The samples containing RS were pulled out from the liquid solution and dried for 1 week at 25°C. Those filled with PN and potassium niobate were dried in a desiccator.

The surface morphology of the porous aluminum oxide films was characterized using a high-resolution scanning electron microscope (HRSEM) operated at low voltages (1.5–4 kV). The crystallographic structure of the films was determined using the Bragg-Brentano X-ray diffraction method operated between 14° and 50°, which covers the main peaks of RS, PN, potassium niobate, and the porous aluminum oxide. The microstructure of the RS crystals inside the pores was characterized by observing vertical cross-section samples with a high-resolution transmission electron microscope (HRTEM). The dielectric properties of the composite film were determined by measuring the polarization as a function of the applied electric field. The aluminum substrate served as one electrode while a second electrode was deposited on top of the composite film. Hence, the electric field was applied along the longitudinal axis of the pores.

3 Results and discussion

3.1 The porous film

The electrochemical anodization of the pure aluminum samples resulted in a porous film. Top view HRSEM images of the porous films show (Fig. 1a–d) a highly-dense array of pores (about 10^{11} cm^{-2}) having a narrow diameter distribution. The average pore diameter can be varied depending on the applied voltage and current. The pores are aligned in vertical to the film plane (Fig. 2) and their length (1.3 μm in our case) can be changed by the anodization time. The XRD spectra of the empty porous film correspond (e.g. Fig. 3a) to crystalline phases [7, 8].

3.2 Growth of single-crystals inside the pores

The presence of single-crystals inside the pores was confirmed using XRD and HRTEM vertical cross-section

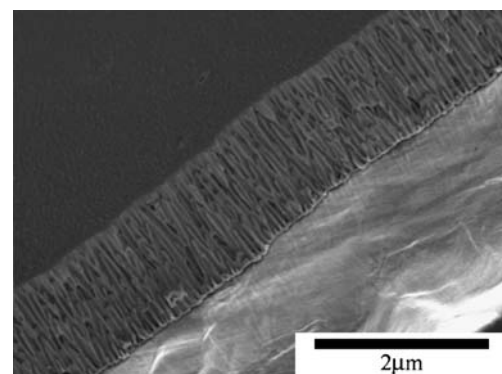


Fig. 2 HRSEM side-view image of porous aluminum oxide grown on electrochemically polished aluminum substrate at around 25°C

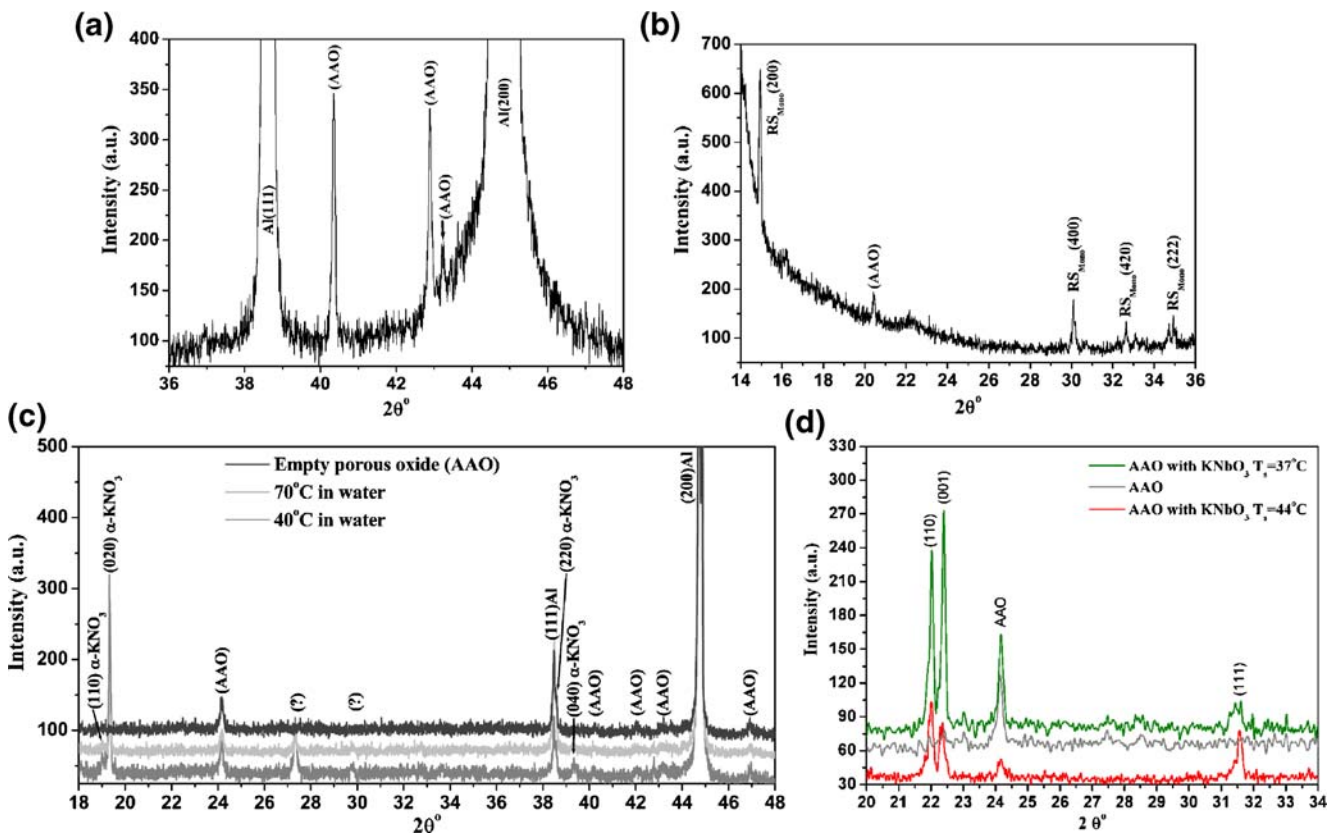


Fig. 3 XRD spectra: (a) Empty porous film grown under constant current conditions. (b) RS-filled AAO film with (200) preferred orientation. (c) PN-filled AAO film with (020) preferred orientation. (d) AAO film filled with potassium niobate crystals

methods. XRD spectrum of the RS-filled porous film (Fig. 3b), shows peaks which solely correspond to the RS monoclinic phase. The intensity of the (200) peak is almost one order of magnitude higher compared to the other RS peaks, indicating a preferred crystallographic orientation of

the RS crystals in the pores towards the [100] direction, which is the polarization direction of the ferroelectric phase.

The preferred orientation of the RS crystals within the pores was also confirmed by TEM studies. A Selected area electron diffraction pattern taken from the RS-filled aluminum oxide film (vertical cross-section area that

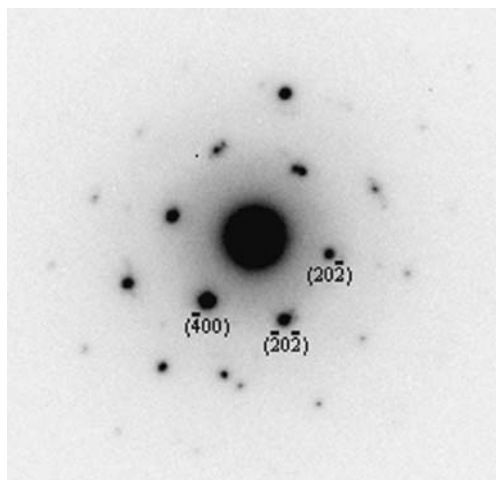


Fig. 4 An electron diffraction pattern, taken from a vertical cross-section area containing 25 RS-filled pores, indicating a uniform crystallographic orientation characterized by a single zone-axis pattern

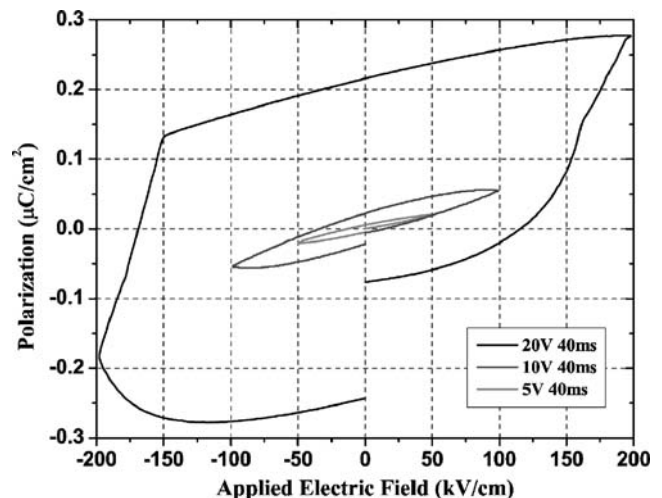


Fig. 5 Polarization vs. applied electric field for various voltages at 25 Hz for PN-filled porous aluminum oxide composite film

contained approximately 25 pores) reveals a dot-pattern corresponding to the monoclinic phase of the RS crystals (Fig. 4). The dot-pattern, corresponding to a single zone axis [010], indicates a uniform crystallographic orientation of the RS crystals within the pores. These crystals exhibit enhanced polarization and thermal stability of the ferroelectric phase [9].

The XRD spectrum of the PN-filled porous film (Fig. 3c) shows two peaks which correspond to the non-ferroelectric orthorhombic phase. At a saturation temperature of 70°C the (110) peak has a negligible intensity, while the intensity of the (020) peak is much higher. In addition, the (020) peak has a relative intensity of only 11% in the case of randomly oriented powder. Hence, there is a pronounced preferred crystallographic orientation of the PN crystals in the pores towards the [010] direction. Decreasing the saturation temperature to about 40°C improves the preferred [010] orientation.

The PN crystals within the pores exhibit unique dielectric behavior which is characterized by an electric field induced phase transition. At low applied electric fields (below 50 kV/cm) the dielectric behavior is relatively linear, while at higher applied electric fields (above 100 kV/cm) the dielectric behavior is non-linear (Fig. 5). Since the bottom electrode is separated from the crystals by a thin aluminum oxide film (about 30 nm) called the barrier layer, which is formed during the anodization process, and is not directly connected to the crystals, a pseudo-capacitor arrangement is formed, and an unknown portion of the applied electric field drops on the oxide layer. This also leads to a lossy behavior and lack of polarization saturation as can be seen in Fig. 5.

The change in the dielectric behavior can be attributed to a phase transformation from the non-ferroelectric orthorhombic α -phase to the ferroelectric rhombohedral γ -phase. There is no record in the literature regarding electric field induced phase transition in bulk PN. In our case, the phase transformation is attributed to a combined effect of hydrostatic pressure applied by the pore walls [10] and the applied electric field.

Even for potassium niobate, which is almost insoluble in water, crystals grew inside the pores. Moreover, they have preferred crystallographic orientations which correspond to the (110) and (001) planes (Fig. 3d). The influence of temperature on the growth direction is similar to that seen for PN, meaning that increasing the solution temperature decreases the preferred orientation.

In all the cases described above, preferred crystallographic orientations of the crystals grown within the pores were observed. The precondition for preferred orientation in our case is preferred nucleation on the bottom of the pores, which is determined by pore radius of curvature, and pore diameter [11]. In addition, the growth from a supersaturated aqueous solution should be done by precipitation under thermodynamic conditions close to the saturation temperature.

4 Summary

This paper presents experimental evidence for the formation of nano-rods of single-crystals with preferred crystallographic orientations inside aluminum oxide porous film. The experimental results show RS and PN single-crystals having their [100] and [010] crystallographic orientations, respectively, along the longitudinal axis of the pores. Preferred orientation was obtained also for potassium niobate. Formation of these crystals requires preferred nucleation at the pore bottom, and growth under exact thermodynamic conditions, which are achieved by precisely controlling the saturation temperature and the cooling rate. These single crystals exhibit unique dielectric properties and thermal stability.

References

- O. Boni, S. Berger, *J. Nanosci. Nanotechnol.* **1**, 433 (2001)
- E.D. Mishina, K.A. Vorotilov, V.A. Vasil'ev, A.S. Sigov, N. Ohta, S. Nakabayashi, *J. Exp. Theor. Phys.* **95**, 502 (2002)
- F.D. Morrison, Y. Luo, I. Szafraniak, V. Nagarajan, R.B. Wehrspohn, M. Steinhart, J.H. Wendorff, N.D. Zakharov, E.D. Mishina, K.A. Vorotilov, A.S. Sigov, S. Nakabayashi, M. Alexe, R. Ramesh, J.F. Scott, *Rev. Adv. Mater. Sci.* **4**, 114 (2003)
- B.A. Hernandez, K.S. Chang, E.R. Fisher, P.K. Dorhout, *Chem. Mater.* **14**, 480 (2002)
- S.S.N. Bharadwaja, M. Olszta, S. Trolier-McKinstry, X. Li, T.S. Mayer, F. Roozeboom, *J. Am. Ceram. Soc.* **89**, 2695 (2006)
- A. Marmur, *J. Colloid Interface Sci.* **129**, 278 (1989)
- G.E. Thompson, G.C. Wood, *Nature* **290**, 230 (1981)
- G.E. Thompson, R.C. Furneaux, G.C. Wood, J.A. Richardson, J. S. Goode, *Nature* **272**, 433 (1978)
- D. Yadlovker, S. Berger, *Phys. Rev. B* **71**, 184112 (2005)
- A.N. Morozovska, E.A. Eliseev, M.D. Glinchuk, *Phys. Rev. B* **73**, 214106 (2006)
- D. Yadlovker, S. Berger, *J. Appl. Phys.* **101**, 034304 (2007)