Highly Sensitive Piezoelectric Response of Sodium Nitrite Nano-crystals to Low Applied Mechanical Pressures

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Abstract: Development of highly-sensitive detectors of low mechanical pressures in the scale of few Pascal and below in environmental conditions are of a high technological demand for a variety of applications such as a remote control of infants breathing and a leakage alert of hazardous gases. This paper reports on a highly sensitive piezoelectric detector of low applied mechanical pressures down to 0.1 Pa in atmospheric environment ($10^{-4}\%$ pressure change). It is made of SN (sodium nitride) nanocrystals grown inside alumina pores with a preferred crystallographic orientation that can be controlled by their formation conditions based on a thermodynamic driving force. The SN nanocrystals inside the pores show a piezoelectric current response to low applied mechanical pressure which depends on the crystallographic orientation of the crystals and the level of residual or applied static strains. The piezoelectric current response is correlated with the unique molecular structure of the SN crystals.

Key words: Sodium nitrite, crystal growth, piezoelectric, pressure detector, preferred crystallographic orientation.

1. Introduction

Detection of ultra-low mechanical pressure changes in the range of few Pascal in an atmospheric environment is of high a technological interest in various applications such as a remote infants breathing monitoring [1], a leakage alert of hazardous gases [2], a mechanical stability control of intelligent systems [1] and acoustic propagation disturbances [3]. A substantial progress in detection of low mechanical pressure changes has been achieved during the last decade through various methods [1]. The piezoelectric detection method has many advantages owing to its passive detection mode, low energy consumption [4], high sensitivity and fast response [5]. Increasing piezoelectric detection sensitivity requires materials having a small crystal size in the nanometer scale, a low dielectric permittivity to gain a high figure-of-merit value in converting a mechanical

energy to an electric energy and a low dielectric noise [6, 7], and uniform crystallographic orientation of the crystals having the polar axis oriented in the detection direction.

Among the low-k piezoelectric materials, SN (sodium nitrite) has a high potential for a sensitive piezoelectric detection due to its planar molecular structure consisting of a negatively charged covalent nitrite group connected ionically to a sodium ion [8]. The room temperature orthorhombic unit cell structure of SN crystals is stable up to 162 °C [9] having a spontaneous dielectric polarization along the [010] direction [9, 10]. SN nano-crystals are usually grown inside a porous array of AAO (anodized aluminum oxide) or a porous glass [11-13]. However, no preferred crystallographic orientation is reported for these nano-crystals. The piezoelectric coefficients of bulk SN single crystal have been reported experimentally [14] to be in the range of 0.7-3.3 pC/N. These piezoelectric coefficient values are comparable to those reported of AlN thin films [15].

This paper reports on a highly sensitive

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piezoelectric current response of SN nano-crystals to applied mechanical pressures as low as 0.1 Pa in an atmospheric environment. It shows the dependence of the piezoelectric current response on the crystallographic orientation of the SN nano-crystals at different levels and types of residual strains and explains it based on atomic movements in the unique SN molecular structure. The ability to control the crystallographic orientation of the SN nano-crystals is proven and explained based on a thermodynamic driving force.

2. Experimental

SN crystals growth was performed by precipitation from a liquid solution inside nano-pores of AAO. Prior to the crystal growth process the porous substrate was prepared: Aluminum disks having a thickness of 0.1 mm and a diameter of 20 mm were mechanically polished to a roughness level of 10 nm. The AAO porous layer is obtained at room temperature by electrochemical anodization of the polished surface in a 0.3 M oxalic acid aqueous solution at an applied electric field of 40 V/cm for 2 hours. The AAO porous layer was treated in a phosphoric acid (5 wt.%) aqueous solution by applying an electric field of 10 V/cm for 40 minutes to enlarge the diameter of the alumina pores.

The Al substrates with the AAO porous layers were inserted to unsaturated aqueous solutions that contain SN at different concentrations (6-8 gr SN/10 gr H₂O) at room temperature. The substrates were held inside the aqueous solutions for 20 hours. At the end of the process the substrates were pulled out from the aqueous solutions and their surfaces were delicately wiped from any residual material. A top electrical contact on the outer surface of the porous layer consists of e-gun evaporated 100 nm thick silver layer having a 4 mm diameter. The back side of the Al substrate was used as a back electrical contact. Cu-Sn wires bonded with a silver paste to the electrical contacts on the samples connected the samples to the

measuring instruments.

The surface morphology and thickness of the porous AAO layers were characterized using a HRSEM (Zeiss Ultra-plus FEG). XRD (Rigaku Smart Lab) was used in the Bragg-Brentano configuration to identify the phase type and orientation of the SN crystals grown inside the pores. Low mechanical pressure of 0.1-10 Pa was applied by directing an air stream to the center of the sample while its two opposite edges are clamped (Fig. 1a). The air flow rate is controlled by a mass flow controller. The level of the mechanical pressure applied on the sample is measured and calibrated using a highly sensitive and calibrated weight device (sensitivity of 0.05 mgr, Adventurer—OHAUS). The piezoelectric current response is measured simultaneously with the applied dynamic mechanical pressure by using a sensitive electric current meter (Keithley 6154 System Electrometer) connected to an oscilloscope. The piezoelectric current response of the SN nanocrystals was also studied while the samples were subjected to static strains generated by bending the substrate (Fig. 1b), the strains due to bending were calibrated by strain-gauge.

3. Results

HRSEM top view images (e.g. Fig. 2a) show a highly dense array of pores on the surface of substrate. The average diameter of the pores is 55 nm and the diameter distribution is presented in Fig. 2b. A HRSEM vertical cross section view of the porous layer (Fig. 2c) reveals that the pores are aligned in-vertical to the porous layer plane having a uniform diameter along their 10 μ m depth. The pores' walls are made of an amorphous alumina having a thickness of about 40 nm. The bottom of the pores is closed by the alumina walls (Fig. 2d) with a small radius of curvature.

XRD diffraction patterns of the porous layer filled with the SN material show preferred crystallographic orientations of the orthorhombic SN phase (according

Fig. 1 Schematic illustration of the experimental system. (a) Setup of applying pressure: Sample is tow clamped at opposite edges; its center is exposed to air pressure through a needle. Intensity of the air pressure is controlled by mass flow controller; its modulation is made by chopping the air flow by a rotating perforated wheel. (b) Setup of generating strains: One edge if the clamped specimen is fixed, the other edge moves by a stepper-motor that is driven by a computer, consequently the sample is bended, amount of displacement is measured by micrometer.

to the ICDD card #00-006-0392) along the longitudinal axis of the pores in-vertical to the porous layer plane (Fig. 3). The preferred crystallographic orientation of the SN crystals is controlled by the concentration of the liquid solution. The SN crystals grown in the liquid solution concentration of 6 [gr SN/10 gr H₂O] have their polar axis [020] oriented in-vertical to the porous layer plane (Fig. 3a). (This sample is called “polar-oriented”). The SN crystals grown in the liquid solution concentration of 8 [gr SN/10 gr H₂O] have their polar axis [020] oriented parallel to the porous layer plane (Fig. 3c). (This sample is called “non-polar-oriented”). The SN crystals grown at the liquid solution concentration of 7 [gr SN/10 gr H₂O] have two XRD peaks having the same height and area (Fig. 3b). The first peak corresponds to crystals having their polar axis oriented in-vertical to the porous layer plane and the second peak corresponds to the SN crystals having their polar

axis oriented in-parallel to the porous layer plane. (This sample is referred to as “mix-oriented”).

Applying an alternating mechanical pressure on the different samples created an alternating electric current response. A linear relationship between the amplitude of the electric current and the magnitude of the applied mechanical pressure is obtained and characteristic to a piezoelectric effect (Fig. 4). The piezoelectric current response is more significant and almost the same in the “polar-oriented” and “non-polar-oriented” SN nanocrystals than that of the “mix-oriented” sample (Fig. 4). The “polar-oriented” sample was found to be the most piezoelectric sensitive capable of detecting an applied mechanical pressure of 0.1 Pa as compared to 1 Pa of the “non-polar” and “mix-oriented” samples. The small applied mechanical pressures were achieved experimentally by increasing the distance between the air flow nozzle and the samples. (The magnitude of

Fig. 2 (a) A top view HRSEM image of the porous layer; (b) The diameter distribution of the pores with an average diameter of about 55 nm; (c) A vertical cross section view of the porous layer showing a 10 μm thickness of the AAO porous layer; (d) A vertical cross section view of the bottom of pores.

the applied pressure below 1 Pa was estimated by a linear extrapolation of the calibrated values to the measured electric current response, since no calibrated devices in this range are available in our lab).

The effect of applied static compressive strain in the porous layer plane on the piezoelectric current response of the SN crystals is shown in Fig. 5. The “mix-oriented” sample does not show any change of the piezoelectric current response due to increasing the static compressive strains in the range of 0-60 $\mu\text{-strain}$. The “polar oriented” sample shows a sharp increase of the piezoelectric current response with increasing the static compressive strain up to 30

$\mu\text{-strain}$ and then it reaches a constant value in the range of 30-60 $\mu\text{-strain}$. The “non-polar-oriented” sample shows a linear decrease of the piezoelectric current response with increasing the static compressive strain from 0 to 60 $\mu\text{-strain}$.

4. Discussion

The SN crystals nucleate and grow inside the pores due to precipitation of the solute ions from a saturated liquid solution. The liquid concentrations at which the SN crystals were grown inside the pores are lower than the saturation concentration value determined outside the pores (Table 1). This result indicates a higher

Fig. 3 XRD patterns of the SN crystals grown inside the porous layer at different liquid solution concentrations. Arrows indicate the polar direction relative to the porous layer plane. (a) SN crystals with a preferred crystallographic orientation of the polar axis in-vertical to the porous layer plane; (b) SN crystals with two preferred crystallographic orientations of the polar axis in-vertical and in-parallel to the porous layer plane; (c) SN crystals having a preferred crystallographic orientation of the polar axis in-parallel to the porous layer plane.

Fig. 4 The effect of alternating applied mechanical pressure on the piezoelectric current response (current-time plot). The piezoelectric current magnitude for different pressure values in: (a) “polar-oriented”; (b) “mix-oriented”; (c) “non-polar-oriented” samples.

Fig. 5 The effect of applied static compressive strain on the piezoelectric current response of (a) the “polar-oriented”; (b) the “mix-oriented”(“non-polar-oriented”); (c) “non-polar-oriented” (“mix-oriented”) SN nanocrystals.

Table 1 The liquid solution concentrations at which SN crystals have grown inside the alumina pores and the preferred crystallographic orientation of the SN crystals in the direction of the longitudinal axis of the pores. The bulk saturation value of the liquid solution outside the pores is given at the last row in the table.

Liquid concentration [gr SN/10 gr H ₂ O]	Preferred crystallographic plane	Unit cell atomic arrangement
6	(200)	
7	(200) + (020)	
8	(020)	
8.5—bulk solute saturation		

solute concentration inside the pore than the saturation value while the solute concentration outside the pores is below the saturation value. The enhanced solute

concentration inside the pores can be attributed to a surface energy effect [16]. The small diameter of the pore (55 nm) creates a curved surface at the cylinder

shape of the pore walls and at the sphere shape at the bottom of the pore. The surface energy decreases with decreasing the surface radius of curvature, especially in the nanometer scale as in our case, leading to an increase of the liquid solute concentration adjacent to the curved surface [17-19]. The maximum concentration of the solute ions in the liquid solution is expected to be at the bottom of the pore site where the local surface radius of curvature is the smallest compared to all sites of the pore walls surface, as seen in Fig. 2d and illustrated in Fig. 6. The nucleation begins at the liquid/solid interface at the bottom of the pore due to precipitation of solute ions from a higher liquid concentration than the saturation value. The first crystallographic plane formed at the solid/liquid interface determines the crystallographic orientation of the SN crystals that grow from the bottom of the pore upward along the longitudinal axis of the pores.

The XRD pattern analysis shows (Fig. 3 and Table 1) that the SN crystals have a high preferred crystallographic orientation in the direction of the longitudinal axis of the pores which depends on the liquid concentration. At the liquid concentration of 8 [gr SN/10 gr H₂O], the SN crystals inside the pores have their (020) planes formed at the liquid/solid interface at the bottom of the pores creating a highly crystallographic oriented SN crystals along the

longitudinal axis of the pores. At the liquid concentration of 6 [gr SN/10 gr H₂O], the SN crystals inside the pores have their (200) planes formed at the liquid/solid interface at the bottom of the pores creating a highly crystallographic oriented SN crystals along the longitudinal axis of the pores. At the liquid concentration of 7 [gr SN/10 gr H₂O] both (020) and (200) preferred crystallographic orientations are obtained indicating a partial transition from the (020) to the (200) crystallographic orientation. The increase of the liquid concentration increases the supersaturation concentration of the solute ions in the liquid solution at the bottom of the pore, consequently creates a higher excess energy for precipitation of solute ions [19] and leads to formation of crystallographic planes that need a higher formation energy (due to a higher number of sodium atoms associated with the crystallographic plane (4 in the (020) plane vs. 1 in the (200) plane) (Table 1), but probably a more thermodynamically stable. The low concentration of solution decreases the supersaturation in the liquid solution at the bottom of the pore and creates a low excess energy for precipitation of solute ions [19], this leads to formation crystallographic planes with low formation energy, but probably favorable kinetically (due to a neutrality of the 200 planes). An intermediate concentration of the growth

Fig. 6 A schematic illustration of the solute concentration gradient inside the alumina pore. R and C indicate the radius of curvature and concentration of solute, respectively. A higher concentration of the solute is present in the vicinity of the curved surfaces due to a surface energy effect.

solution causes a competition between the two considerations.

The applied mechanical pressure results in a piezoelectric current response in all of the studied samples. The crystallographic orientation of the SN crystals affects the piezoelectric response (Fig. 4) where the maximum response is obtained in the “polar-oriented” sample which is slightly higher than that obtained in the “non-polar-oriented” sample while the minimum response is obtained in the “mix-oriented” sample. This behavior is explained in the following text. The applied mechanical pressure on the sample leads to its bending, as described in Fig. 7, since the sample is clamped in its two edges. Consequently, a compressive strain is formed in the porous layer plane including the SN crystals inside the pores. The alternating applied mechanical pressure creates an alternating magnitude of the compressive strain in the porous layer plane (Fig. 7a). In the “non-polar-oriented” sample, where the SN crystals have their polar axis oriented parallel to the porous layer plane, the compressive strain results in a

decrease of the distance between the positively charged sodium ion and the negatively charged nitrite group in the direction of the polar axis [20], leading to a decrease of the dielectric of the dipole magnitude and the consequent piezoelectric current response which is measured in vertical to the porous layer plane (Fig. 7c). In the “polar-oriented” sample, where the SN crystals have their polar axis oriented in-vertical to the porous layer plane, the compressive strain in the porous layer plane results in an increase of the distance between the nitrite group and the sodium ion along the direction of the polar axis [20]; this causes an increase in the dielectric dipole magnitude and the piezoelectric current response that flows in the opposite direction to that formed in the “non-polar-oriented” sample (Fig. 7b). In the “mix-oriented” sample, the direction of the dielectric dipoles in the “polar-oriented” SN crystals is opposite to that in the “non-polar-oriented” SN crystals leading to a reduction of the net dipole moments and piezoelectric current response in one direction (Fig. 6d).

Fig. 7 (a) Modulation of the compressive in-plane pressure applied on SN nanocrystals inside pores. Piezoelectric current in response to the same pressure has opposite direction in (a) (should be (b)) “polar-oriented”; (b) (should be (c)) “non-polar-oriented” SN, due to opposite movements of atoms in unit cell; (d) modulation of current in “mix-oriented” SN is a vector summation of both orientations.

The effect of the applied static compressive strain on the piezoelectric response (Fig. 5) is explained in the following text. In the case of the “polar-oriented” sample (Fig. 5a), the applied static compressive strain shifts the oxygen atoms towards each other increasing the Na-NO₂ bond length and the piezoelectric current response in the same direction as that without the applied compressive static strain. The piezoelectric current response reaches a constant maximum value (Fig. 4a) when the Na-N and/or O-N-O bond length reaches its maximum elastic strain. In the case of the “non-polar” sample, the applied compressive static strain results in an opposite atoms movement namely a decrease of the Na-NO₂ bond length and an increase of the O-N-O bond length leading to a piezoelectric current response in the opposite direction than that without the applied static compressive strain and a total decrease of the piezoelectric current response (Fig. 5b). In this case, the piezoelectric current does not reach a constant value since the bonds lengths do not reach their maximum elastic strain. In the case of the “mix-oriented” sample, the piezoelectric current response is a superposition of the two opposite piezoelectric current response directions leading to very small value (Fig. 5c).

The best sensitivity to a small compressive applied mechanical pressure is obtained in the case of the “polar-oriented” sample under no applied static compressive strain. This result indicates that a higher sensitivity is obtained when the Na-N bond length is not under any elastic constrain and their electric attraction force decays as they move apart from each other.

5. Summary

SN nanocrystals were grown inside AAO porous layer with preferred crystallographic orientations that can be changed with the concentration of the liquid solution. The SN crystals inside the pores show a piezoelectric current response to applied mechanical pressure as low as 0.1 Pa in environmental atmosphere

conditions (10⁻⁴% sensitivity). The crystallographic orientation of the SN crystals has a major effect on their piezoelectric current response and sensitivity. The presence of a compressive residual strain decreases the piezoelectric current response sensitivity.

Data Availability

The raw and processed data required to reproduce these findings are available with the manuscript.

Declarations of Interest

None.

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