OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 4, No. 12, December 2010, p. 1984 – 1986

Hydrothermal synthesis of $Si_{1-x}Sn_xO_2$ single crystal

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The interest of $Si_{1-x}Sn_xO_2$ single crystals with alpha-quartz structure is connected to improvement of electromechanical coefficients and rise of α – β phase transition of quartz one. For first time, growth of an α - $Si_{1-x}Sn_xO_2$ crystal was realized by a hydrothermal method of temperature gradient in autoclaves, made from Cr–Ni alloys. Nutrient material was prepared from synthetic quartz as crashed rods and placed in the bottom of autoclaves. There was loaded SnO_2 powder additive in proportions to quartz nutrient. Single crystals were investigated by electron microprobe analysis, X-ray diffraction at room temperature and high temperatures. The most important result, which was obtained during the investigations, is an experimental proof of growth of α- $Si_{1-x}Sn_xO_2$ single crystals under the hydrothermal conditions. The present results thus open the possibility to tune the piezoelectric properties of these materials by varying the chemical composition.

(Received November 22, 2010; accepted November 29, 2010)

Keywords: α-quartz, Hydrothermal, α-β transition, Si-Sn-O, Single crystal

1. Introduction

α-Quartz type materials are of major interest due to their piezoelectric properties. In addition to α-quartz itself, this family is composed of GeO_2 and compounds with the general formula $M^{III}X^{V}O_4$ where M= Al, Ga, Fe, B, and X=P and As. The α-quartz structure, space group *P* 3_121 (or *P* 3_221), is built up of left-handed (or right-handed) helical chains of RO_4 (R=M or X) parallel to the c-axis. Each MO_4 tetrahedron shares its four corners with XO_4 tetrahedra.

Considerable progress has been made in recent years towards understanding the nature of piezoelectric properties in terms of the underlying crystal structure.

For α-quartz structure, the structural distortion present can be described geometrically by rotating rigid tetrahedral around the <100> axes through an angle δ [1]. In the α quartz at room temperature δ is either positive or negative 16.3 ˚, but in the β structure is zero.

The more distortion structure involves increasing δ. One of main way to obtain a more distortion structure, it is to increase the average size of $\langle r_M \rangle$ of M-site cations. The distorsion structure is connected to improvement of electrochemical coefficients and rise of α-β phase transition of quartz ones.

Therefore, in the present paper, the $Si_{1-x}Sn_xO_2$ single crystal with x=0.05, 0.1 were obtained by hydrothermal method and the crystal structure was determined by X-ray diffraction. Also, it was studied the stability of the α-quartz structure and phase transition temperature up to 640°C. These results can be used to tune the piezoelectric properties of these materials by varying the chemical composition.

2. Experimental

The growth of α –$Si_{1-x}Sn_xO_2$ crystals was realized by a hydrothermal method of temperature gradient in autoclaves of 500 cm^3 in volume, made from Cr–Ni alloys. A chemical of 0.5-1.0 M Na_2CO_3 was used as mineralizer. Seeds were cut from synthetic quartz crystals in the shape of plates parallel to the Z-axis and sizes of the seeds were 2 × 10 × 50 mm. Nutrient material was prepared from synthetic quartz as crashed rods and placed in the bottom of autoclaves. There was loaded SnO_2 powder additive in proportions to quartz nutrient.

Temperature has a high influence on Sn-content in α $Si_{1-x}Sn_xO_2$ crystals. With the same relation of quartz and tin dioxide in nutrient , the crystal growth temperature from 350 °C to 370 °C, nutrient dissolution zone temperature rises from 400°C to 420 °C (pressure up to 1300 bar) leads to increasing of SnO_2 content up to 1 %. The temperature gradient was from 30 to 70 °C. The effect of the different growth parameters will be detailed in the following section.

For each crystal, several characterizations were performed. First, the chemical composition was analysed by electron probe microanalysis along the crystal. Then, several pieces were cut from the sample. One of them was crushed and used for X-ray powder diffraction using Cu-Kα radiation, in the range 2θ = 10-100°, at room temperature. High temperature x-ray powder diffraction measurements were performed on a PanAnalytical X'Pert diffractometer equipped with an PixCel detector using Cu K-α radiation. The powder sample was placed in an Anton Par HTK 2000 high temperature chamber. X-ray diffraction data were obtained from 10˚ to 100˚ in 2θ with a 0.01 step size over the range up to 640 °C. The heating rate between point was 10 °C/minute. The phase purity

was checked, and the crystal structure was refined, by using the Fullprof suite [2].

3. Results

Single crystals of length 50 mm (Fig. 1) with the tin content 0.5 and 1 % were grown. Because the solubilized state under hydrothermal conditions remains obscure in many respects, all growth parameters (dissolution temperature, growth temperature, pressure and mineralizer concentration) were studied in terms of tin substituted in the SiO_2 structure. For all the samples of $Si_{1-x}Sn_xO_2$ single crystals , it was obtained a single α-quartz phase (Fig. 2).

Fig. 1. Photograph of grown $Si_{0.99}Sn_{0.01}O_2$ crystal obtained after 7 days, using a temperature gradient of 70 °C, dissolution temperature 420 °C and pressure 1000 bar.

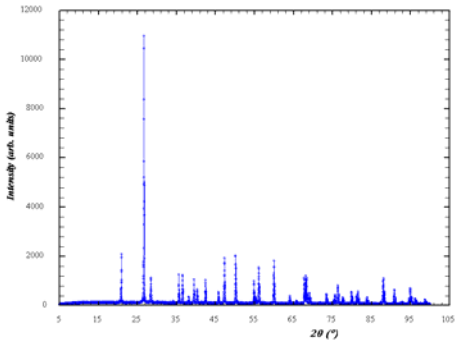

Fig. 2. The X-rays diffraction pattern of single crystal of $Si_{0.99}Sn_{0.01}O_2$ at the growth condition.

The structural data for $Si_{0.995}Sn_{0.005}O_2$ and $Si_{0.99}Sn_{0.01}O_2$ (Table 1) are found to vary continuously as a function of composition.

Table 1. Experimental data – X-ray powder diffraction for $Si_{1-x}Sn_xO_2$ single crystal.

Crystal data	$Si_{0.995}Sn_{0.005}O_2$	$Si_{0.99}Sn_{0.01}O_2$	$Si_{0.99}Sn_{0.01}O_2$
T (K)	296	296	873
Crystal system	Hexagonal	Hexagonal	Hexagonal
Space group	$P3_121$	$P3_221$	$P6_222$
a (Å)	4.9000(1)	4.9160 (1)	4.9977 (1)
c (Å)	5.3900 (1)	5.4054 (1)	5.4601 (1)
V (Å^3)	112.08 (1)	113.13 (1)	118.11 (1)

It was studied the stability of the α-quartz structure and phase transition temperature up to 640°C (Fig. 3).

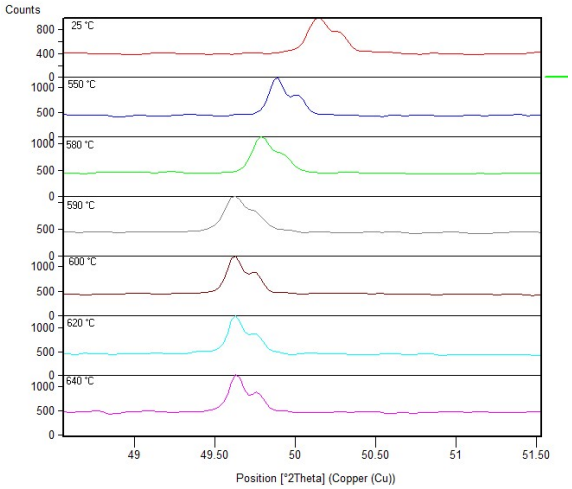

Fig. 3. Selected region in the x-ray diffraction pattern of $Si_{0.99}Sn_{0.1}O_2$ single crystal for different temperatures.

The electron microprobe analysis was performed at different points in the sample and was confirmed the uniformity and the closely stoichiometric composition with the precursor material. Also, electron microprobe analysis has been shown that Z-growth material is desired for the electronic application because the aluminum concentration is very low (up to 5 ppm).

4. Discussion

We found that dissolution temperature and the molarities of Na_2CO_3 solution have a high influence on Sn-content. This can be linked to form the various complexes or species during the hydrothermal crystallization. For identify and quantify such species, the observation of SnO_2-SiO_2-NaOH-H_2O system under high temperature and pressure conditions is necessary. But it is possible like in the quartz case, soluble silicates of forms such as $Si_3O_7^{2-}$ and Si_3O^{2-} or soluble species which contain Sn are formed in the presence of hydroxides. For example, increasing the molarities of Na_2CO_3 solution from 0.5 M to 1 M, in the same growth conditions (420 °C dissolution temperature, 370°C growth temperature and 1300 bar) determines increasing of Sn content from 0.5 % to 1 %. The growth temperature doesn't influence significantly the Sn-content in the same pressure and temperature gradient condition. Growth temperature has an influence on the growth rate (0.4-1.4 mm/day) and the quality of the grown crystals.

For all the samples of $Si_{1-x}Sn_xO_2$ single crystal (x=0.005; 0.01), a single α-quartz phase in the $P3_121$ space group was determined at room temperature. The cell volume is found to vary continuously as a function of composition in according with ionic radius of Si^{4+} (0.26

Å), and Sn^{4+} (0.55 Å), from 111.048 $Å^3$ (x=0) to 113.13 $Å^3$ (x=0.01).

The composition $Si_{0.99}Sn_{0.1}O_2$ was studied up to 640 °C. The structure could be refined using an α-quartz- type structural model (Fig. 2) up to 600 °C. After this temperature, the refinement was performed using β- quartz –type phase (Table 1).

Temperature of the transition α-β of $Si_{1-x}Sn_xO_2$ crystals regularly rise on increasung Sn content. It shows 600 °C for crystal of $Si_{0.99}Sn_{0.1}O_2$, which exceeds quartz ones on 27°C. This result is attractive because only 1% of Sn content increases the transition temperature with 27°C.

5. Conclusion

The growth conditions for high quality of the new piezoelectric single crystal obtained by the replace of Si by Sn in the SiO2 structure under the hydrothermal conditions have been determined for first time. Dissolution temperature and molarity of Na_2CO_3 solution have a high influence on Sn-content in α-$Si_{1-x}Sn_xO_2$. Temperature of the transition α-β of $Si_{1-x}Sn_xO_2$ crystals regularly rise on increasung Sn content. It shows 600 °C for crystal of $Si_{0.99}Sn_{0.1}O_2$, which exceeds quartz ones on 27 °C. This result is attractive because only 1% of Sn content increases the transition temperature with 27 °C.

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