PMN-PT Crystal of Less Defects and More Uniformity

Zibo Jiang
Innovia Materials (Shanghai) Co., Ltd.
Shanghai, China
jiang@innoviamaterials.com

***Abstract*—3 inch lead magnesium niobate – lead titanate (PMN-PT) crystal ingots are successfully prepared using Vertical Gradient Freeze (VGF) method. Compared with the traditional Bridgman method, VGF method is expected to give higher yield and lower defects due to sufficient agitation and less thermal shock. As a result, [001] grown and poled PMN-PT crystals typically have electromechanical coupling coefficient k_{33} higher than 0.91, suitable for medical ultrasound imaging applications. Rhombohedral-tetragonal phase transition temperature is measured around 90°C and Curie temperature is measured over 125°C as typical imaging-grade crystals. Adequate agitation during growth also enhances in-wafer property uniformity. Variation coefficients for in-wafer free relative permittivity and electromechanical coupling coefficient k_t is measured at 2% and 1%, respectively.**

***Index Terms*—PMN-PT, relaxor ferroelectric crystal, crystal growth, vertical gradient freeze, ultrasound imaging**

I. Introduction

In recent years, relaxor ferroelectric crystal Lead Magnesium Niobate – Lead Titanate (PMN-PT) crystal products have been used on various application such as medical ultrasound imaging, SONAR, micro-actuation and energy harvesting applications due to high electromechanical coupling coefficient and high piezoelectric coefficient [1, 2, 3].

One of the biggest factors limiting wider application of PMN-PT crystal has been cost. High cost of manufacturing PMN-PT crystal originates from (1) expensive platinum crucible, (2) slow growth, and (3) low yield due to property variation and defects. There is also a strong drive for more uniform crystal from transducer designers. This paper focuses on methods to eliminate property variation and defects and enhance uniformity.

The traditional method to grow PMN-PT crystal has been Bridgman technique where platinum crucible moves downwards relative to the growing furnace, creating a temperature gradient and a moving front of solid/melt in favor of PMN-PT crystal formation and desired crystallographic orientation [4]. Such method has its advantages and challenges. The advantages include process flexibilities where additional features could be added onto the existing furnace, such as continuous feeding. The challenges include the complication of having to control temperature and movement of the crucible simultaneously.

In addition, traditional Bridgman technique faces several yield issues:

a) Formation of poly-crystalline PMN-PT due to undesired temperature profiles and strong interactions between crucible and melt, limiting usable crystal parts.

b) Undesired growth direction due to uncontrolled crystallization speed. When this happens, desired wafers need to be cut at an angle to the growth direction (e.g. {001} wafers need to cut 45° from growth direction of [110] grown crystal), leading to in-wafer property variation [5].

c) Defects in as-grown crystal: including cracks, voids and inclusions. Such defects could be caused by unfavorable radial temperature gradient and thermal shock during crystallization. This is particularly true when there is a drive to grow crystal in larger diameters.

In this paper, the author attempts to address the above yield issues by introducing an improved crystal growth method - Vertical Gradient Freeze (VGF) method in which there is no relative movement between crucible and furnace, and crystallization is achieved by synchronized programming of a series of heaters so that a desired temperature profile moves upward relative to the crucible. Conceptual difference between VGF method and Bridgman method has been laid out in Fig. 1 [6]. Through VGF method, crystallization speed can be more accurately controlled by controlling temperature alone.

In addition, adequate agitation can be introduced by adding a crucible rotation mechanism to homogenize ceramic melt and reduce unfavorable radial temperature gradient.

Built on the top of these concepts, Innovia Materials (Shanghai) Co,. Ltd. has developed VGF crystal growth furnaces with mechanical agitation that are suited to grow PMN-PT crystal. The resultant crystal property and uniformity are discussed.

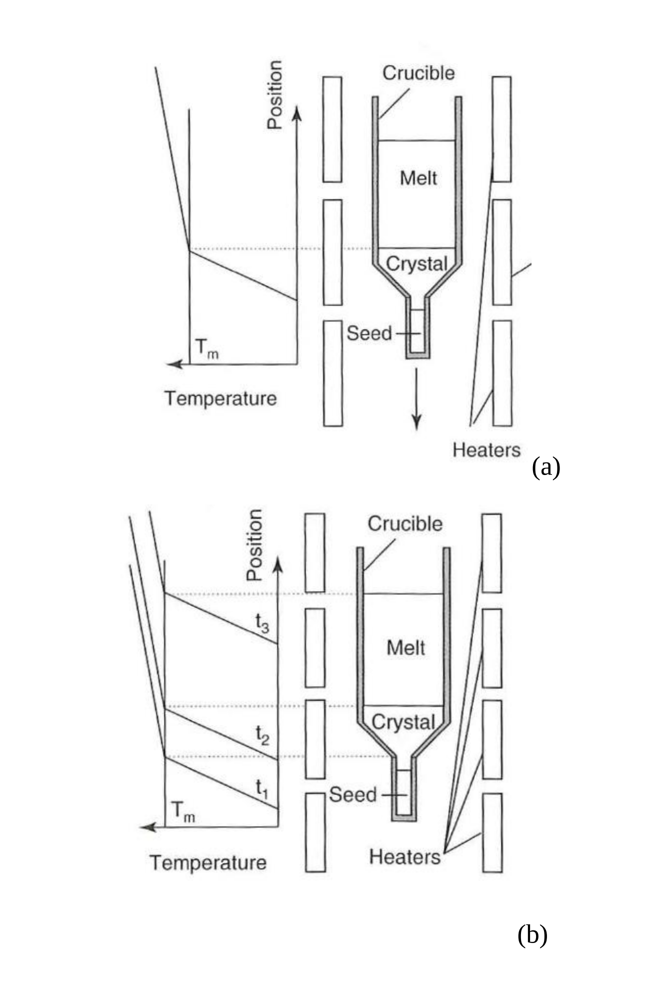


Fig. 1 (a) Bridgman method where crucible moves downward and temperature profile is stationary relative to the heaters, (b) VGF method where crucible is stationary and temperature profile moves upward relative to the heaters [6].

II. EXPERIMENT

73-mm diamemeter PMN-0.31PT ingots were grown using VGF method in platinum crucible with (001) faced seed crystal and precursor ceramic. In each ingot, wafers are selected with faces oriented within 0.5° of the (001) planes (Fig. 2). Plate samples of 10×10×1(H) mm^3 and bar samples of 1×1×5(H) mm^3 were separated from the wafers so that H direction is parallel to the [001] direction. Each sample was sputtered with gold on both faces normal to the [001] direction, followed by poling at room temperature along [001] with a voltage of 3 KV/cm in air. Bar samples were used to determine bar mode coupling coefficient k_{33}; plate samples were used to determine thickness mode coupling coefficient k_t, dielectric constant and transition temepratures. A total of 37 (001) faced wafers were taken from a typical 3'' [001] grown ingot and a total of 10 plate samples were taken from one wafer to represent in-wafer properties.

In accordance with IEEE Standard on Piezoelectricity 176-1987, a Keysight E4990A Impedance Analyzer was used to measure resonance frequency, antiresonance frequency; likewise, capacitance was measured at frequency of 1 kHz at 25° C. Electromechanical coupling coefficient is calculated from Eq. 1, Dielectric cosntant K_3^T is calculated from Eq. 2.

$$k^2 = \frac{\pi}{2}\frac{f_r}{f_a}\tan\left(\frac{\pi}{2}\frac{f_a - f_r}{f_a}\right) \qquad (1)$$

Where k is electromechanical coupling coefficient, f_r is resonance frequency and f_a is anti-resonance frequency.

$$K_3^T = \frac{d}{C}\frac{\varepsilon_0}{A} \qquad (2)$$

where d is sample thickness, A electrode area, C is capacitance, ε_0 is permittivity of space.

Set up for T_c and $T_{R/T}$ measurement is illustrated in Fig. 3. Plate sample is attached to a sample holder which is then wired to Impedance Analyzer. Addtionally, a K-type thermocouple with a temeprature acquisition unit is attached adjacent to the sample. Sample holder is then placed into a programmable oven. Real-time K_3^T-temperature plot is obtained from room temperature to 200 ° C at heating rate of 5° C/min.

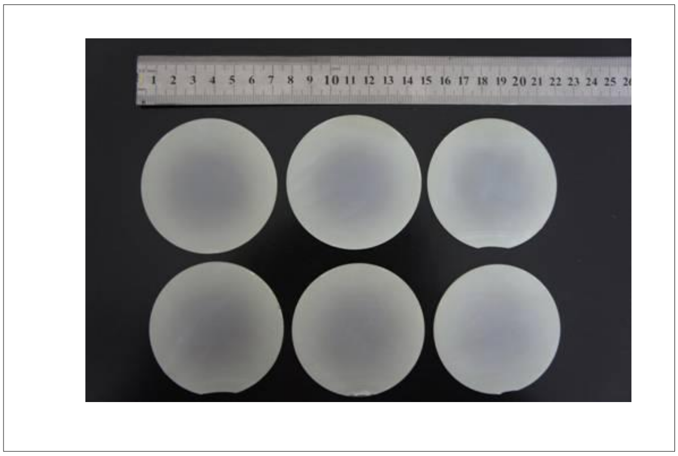
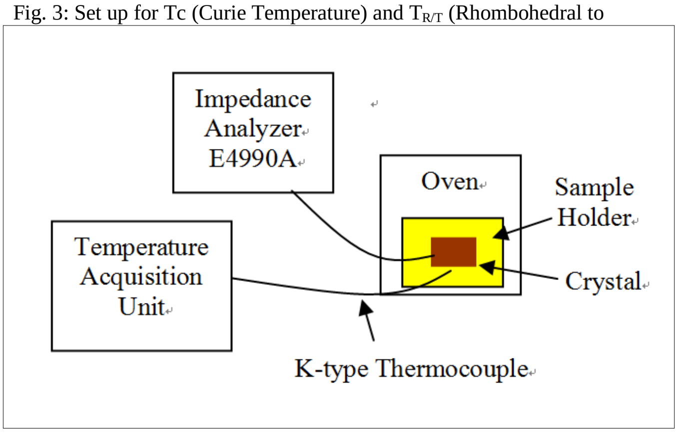


Fig. 2: 73mm-diameter (001) PMN-PT wafers from ingot grown along [001]

Fig. 3: Set up for Tc (Curie Temperature) and $T_{R/T}$ (Rhombohedral to



Tetragonal Transition Temperature) measurement

III. RESULTS AND DISCUSSION

A. In-wafer Uniformity

Table I shows in-wafer properties of dielectric constant and electromechanical coupling coefficient k_t. Average dielectric constant K_3^T is 5389, with variation coefficient of 2%. Average electromecnaical coupling coefficient k_t is 0.59, with variation coefficient of 1%.

TABLE I: IN-WAFER PROPERTY VARIATION

	Typical <001> Wafer PMN-PT Crystal Properties	
Sample #	***Dielectric Constant K_3^T***	***Electromechanical Coupling k_t***
1	5551	0.58
2	5404	0.59
3	5332	0.59
4	5381	0.59
5	5424	0.59
6	5355	0.58
7	5154	0.59
8	5499	0.60
9	5250	0.58
10	5542	0.59
Average	5389	0.59
Standard Deviation	126	0.006
Variation Coefficient	2%	1%

B. Transition Temerpature

Rhombohedral to Tetragonal Transition Temperature $T_{R/T}$ and Curie Temperature T_c of a typical sample in Section III A are denoted in Fig. 4, where $T_{R/T}$ corresponds to the first peak at 93° C and T_c corresponds to the second peak at 132° C.

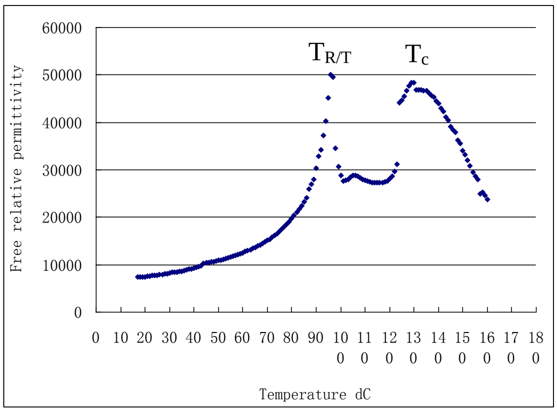
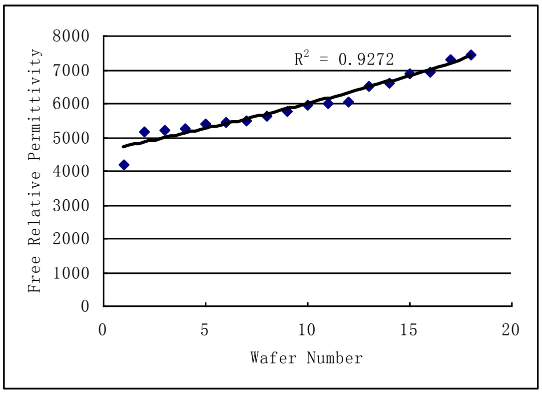


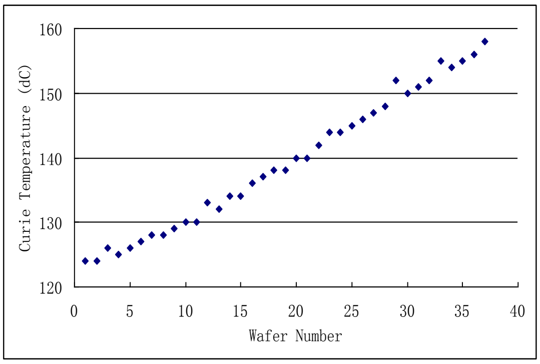
Fig. 4: dielectric constant vs. temperature where T_c and $T_{R/T}$ are denoted

C. Wafer-to-wafer Variation

Wafer-to-wafer variation in terms of dielectric constant K_3^T, curie temperature T_c and electromechanical coupling coefficient k_t are plotted in Fig. 5 (a), (b) and (c).



5 (a)



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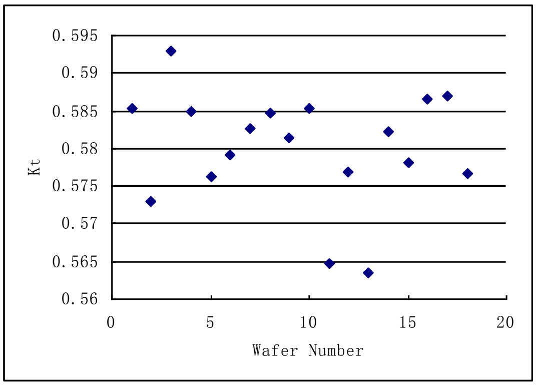

5 (c)

Fig. 5 (a): dielectric constant distribution, (b) Curie temperature distribution and (c) electromechanical coupling coefficient k_t along a typical [001] grown PMN-PT ingot from Innovia Materials. Smaller wafer number represents crystals that crystallize earlier.

From one end of ingot to the other end, monotonic variation is apparent for both K_3^T and T_c, which is attributed to segregation of Tinanium composition across the melt/solid interface. However, this trend is not so apparent for k_t, which is thought to be attributed to the fact that plate dimension has a clamping effect which offsets monotonic variation caused by seggregation [7].

D. Bar mode electromechanical coupling coefficient k_{33}

10 bar samples were taken from lower, middle and higher positions of the [001] grown ingot, respectively, to represent crystals formed at earlier stage, mid-stage and later stage of crystallization. Fig. 6 shows k_{33} values and variations of the three positions. Overall, k_{33} ranges from 0.915 to 0.945 throughout the ingot; crystals which form earlier during crystallization have lower k_{33} values than that form later, which is thought to attributed to the segregation of Titanium composition during crystallization.

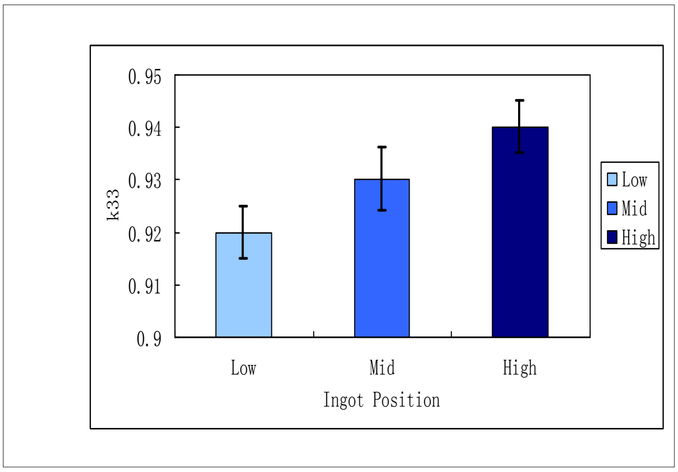

Fig. 6: k_{33} values of <001> PMN-PT from low, middle and higher positions along the ingot

IV. CONCLUSION

Vertical Gradient Freeze (VGF) is an efficient method to manufacture PMN-PT ingot with improved yield. 3 inch PMN-PT ingots grown along [001] were successfully manufactured by Innovia Materials (Shanghai) with the VGF method. As a result, in-wafer property variation has been kept at a low level. However, dielectric constant, bar mode electromechanical coupling coefficient k_{33} and Curie temperature change monotonically from one end of ingot to the other end, attributed from the composition segregation of Titanium during crystallization, which reinforces the importance of using [001] grown ingot for d33 applications, for the sake of better transducer performance. Overall, k_{33} of Innovia (001) PMN-PT crystal ranges from 0.915 to 0.945, dielectric constant ranges from 4600 to 7500, Curie temperature ranges from 125° C to 158 ° C, Rhombohedral to Tetragonal Phase Transition Temperature is measured at around 90° C.

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