Material Parameters of AlN and $LiAlO_2$ Single Crystals

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Abstract— **We have successfully grown high quality AlN piezoelectric single crystal by sublimation technique. Transparent and coloring from amber to dark brown (depending on growth temperature) crack-free boules of approximately 15 mm in diameter and 25 mm in length along [0001] direction were obtained. Full sets of material parameters of grown AlN and commercially available $LiAlO_2$ bulk crystals were measured at room temperature. Temperature coefficients of the material parameters of $LiAlO_2$ were also obtained in a temperature range from 200 K to 310 K.**

I. Introduction

Hexagonal aluminum nitride, AlN (wurtzite structure, 6mm crystal class) is of great interest due to its extreme physical and chemical properties. Attractive piezoelectric properties, very high values of sound velocities and possibility to operate in harsh environment make AlN a very promising material for SAW and BAW applications like resonators, filters and various sensors. AlN does not undergo any phase transition up to its melting point (more than 2000^0 C). As expected, piezoelectric response in AlN can be observed up to very high temperatures. Other benefits of aluminum nitride are high thermal conductivity (2.85 W/cm·K), high electrical resistivity (10^{11}-10^{13} Ω·cm – direct semi-insulating material), transparency in the UV range, small mismatches of lattice constants and thermal expansion coefficients with respect to GaN, etc.

Elastic and piezoelectric constants of AlN were predominantly obtained using AlN thin films on different substrates [1-3] because up to date, only thin films were successfully grown and used for manufacturing of SAW and BAW devices. A set of "stiffened" (i.e., derived without taking into account piezoelectric coupling) elastic constant measured on AlN single crystal using Brillouin light scattering is reported in [4]. All piezoelectric constants and the elastic constant C_{44} were measured using SAW technique in high quality bulk single crystal AlN [5, 6]. Recently, a set of material parameters including elastic and piezoelectric constants of AlN single crystal grown by the physical transport method was evaluated using ultrasonic microspectroscopy technology [7].

Tetragonal (422 crystal class) $LiAlO_2$ single crystals are attracting much attention as a potential substrate for growing III-nitrides like mentioned above AlN and GaN which are technologically very important materials due to their unique physical and chemical properties. Since $LiAlO_2$ shows high sound wave velocities [8, 9] and (due to the symmetry) piezoelectric response, it might be a potential candidate for acoustic applications. Noting that published values of room temperature elastic constants for $LiAlO_2$ are contradictory [8, 9]. To our best knowledge temperature dependent material parameters of $LiAlO_2$ are not measured up to now.

In this communication, we report on the measurements of the dielectric, elastic and piezoelectric constants of AlN and $LiAlO_2$ bulk single crystals at room temperature. Temperature coefficients of the material parameters of $LiAlO_2$ are also presented.

II. Crystals Growth and Samples Preparation

Recently we have developed a production technology based on Physical Vapor Transport (PVT) method for growth of AlN bulk single crystals. The technology involves preparation of large high-purity polycrystalline AlN sources, preparation of high-quality single-crystal AlN seeds, and PVT growth of bulk AlN single crystals. Preparation of the AlN sources utilizes sublimation-recondensation of a commercially available AlN powder which allows removing intrinsic impurities, including poorly removable oxygen. The crystals are seeded using polished single crystalline AlN wafers prepared from the previous special seed grown. Our technology of sublimation growth of AlN bulk crystals includes several stages as follows:

- pre-growth processing: preparation of durable tungsten and pre-carbonized tantalum crucibles, high-purity AlN sources and high-quality SiC seeds;

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- seeding and initial sublimation growth of 2-3 mm long AlN single-crystal layers on SiC seeds in TaC crucibles in graphite equipment;
- separation of the grown single-crystal AlN layers from the SiC seeds and mounting them on the lids of tungsten crucibles;
- sublimation growth of bulk AlN crystals on the single-crystal AlN layers in tungsten crucibles and equipment.

As a result, transparent and coloring from amber to dark brown (depending on growth temperature) AlN boules free of cracks and macroscopic defects with a final length along [0001] (c-direction) up to approximately 25 mm and diameter of 15 mm were obtained. EDS analysis of the elemental composition has revealed that no impurities with concentrations of more than 100 ppm are available in the crystals. More precision analysis with GDMS has revealed an oxygen concentration in the source lower than 10 ppm. Crystallographic quality of the crystals was studied with X-ray diffractometry and topography. Rocking curves in the θ-$2\text{-}\theta$ scan prove that *c*-parameter of the crystal lattice corresponds to that of pure AlN (c = 4.982 Å) and does not vary over the whole crystal. FWHMs of the rocking curves in the ω-scan normally lie in the range 2-6 arc minutes. Rocking curves exhibit also some broadening of the peaks due to the possible elastic strains in the crystals.

Czochralski grown $LiAlO_2$ single crystals were obtained from CrysTec (Berlin, Germany). Cubes with 15 x 15 x 15 mm^3 size oriented along principal [100], [010] and [001] directions are easily available.

For the ultrasonic wave velocity measurements two AlN samples were cut from the as grown boules: i) parallelepiped of 11.7 x 9.5 x 9.5 mm^3 size with the edges parallel to c-, a- and b-axes, respectively, and ii) 45^0 to c-axis thick plate with the length l = 8 mm. For the dielectric studies, thin plates of c- and b-cuts with the averaged dimensions of 8 x 5 x 0.5 mm^3 have been used. The same c-cut plate has also been used for the thickness resonance measurements.

For the determination of all elastic and piezoelectric constants of tetragonal $LiAlO_2$ crystal cubes of approximately 8 x 8 x 8 mm^3 size were prepared in three different orientations: j) with the edges parallel to [100], [010] and [001] directions, jj) [110]-cut and jjj) [011]-cut samples. Again, dielectric measurements were carried out using [100] and [001] plates of 10 x 10 x 0.5 mm^3.

All the samples were carefully ground followed by fine lapping or polishing to achieve parallelism and flatness of the opposite faces. Gold electrodes of 200 nm thickness have been deposited on the big opposite faces of the plates for dielectric measurements.

III. EXPERIMENTAL

Measurements of the bulk acoustic wave velocities propagating along certain crystallographic directions were carried out by a RITEC Advanced Ultrasonic Measurement System RAM-5000. The system realizes pulse-echo method of time propagation measurements using phase detectors with accuracy better than 10^{-4}. To generate longitudinal and shear ultrasonic waves, Y+36^0- and X-cut $LiNbO_3$ transducers of 10 MHz central frequency were used. A special attention was paid to the couplant materials to bond the transducer to the sample, especially in the case of shear modes. The resonance and antiresonance frequencies of the fundamental and first three odd harmonic overtones of the thickness modes of thin c-cut AlN plates were measured using a HP 8753C Network Analyzer. Dielectric measurements were performed using a Solartron SI 1260 Impedance/Gain-Phase Analyzer. All temperature dependent measurements were done using a continuous flow Oxford cryostat in the 220 K to 310 K range with an accuracy and stability of 0.1 K.

IV. RESULTS: ALN

The elastic stiffness coefficients C_{ij} and piezoelectric stress constants e_{ij} can be derived using a system of relations between sound velocities measured at different directions for different modes for 6mm symmetry class crystals [10] assuming the mass density ρ and components of the dielectric constant tensor ε_{ij} are known. Sound velocity measurements (both longitudinal and shear modes) on sample i) provide the following elastic and piezoelectric constants: C_{11}, C_{33}^D, C_{44}, C_{44}^D, $C_{66} = ½(C_{11} – C_{12})$, e_{15}, where $C_{33}^D = C_{33} + e_{33}^2/\varepsilon_{33}$ and $C_{44}^D = C_{44} + e_{15}^2/\varepsilon_{11}$. Measuring the fundamental and odd overtone frequencies of the c-cut electroded plates one can get the corresponding electromechanical coupling coefficient by the overtone ratio method [11], as well as elastic constant C_{33} and piezoelectric stress constant e_{33}. Since the ultrasonic pulse-echo method provides the most reliable results, simultaneous use of both pulse-echo and resonance methods resulted in better reliability and accuracy of the obtained data. The remaining constants C_{13} and e_{31} were determined from the measurements of the sound velocities (quasi-longitudinal and quasi-transverse waves) on sample ii). The relationships between the sound velocities and the elastic constants taking into account also piezoelectric coupling in this case are rather complex [10]. As a result the errors for C_{13} and e_{31} values exceed the errors for C_{11}, C_{12}, C_{44}, C_{33}, e_{15} and e_{33} constants obtained from the sound velocities or resonance frequencies related to simple relations between the wave velocities and elastic constants. Table I summarizes the elastic, piezoelectric and dielectric constants at room temperature (T = 298 K) together with the published data [1 – 7] for single crystalline and thin film samples. The results obtained are generally in a good agreement with published data for single crystals [4–7] except piezoelectric constants e_{33} and e_{31} which are somewhat less and somewhat more, respectively, as compared to the values published in [7]. These differences are probably due to different crystal quality including possible elastic and piezoelectric inhomogeneities of the samples under study as well as different measurement accuracy of various experimental methods: Brillouin light scattering [4], SAW [5, 6] and BAW techniques and ultrasonic microspectroscopy technology [7].

V. RESULTS: $LIALO_2$

Again, the elastic stiffness C_{ij} and piezoelectric stress constant e_{14} can be derived using a system of relations between sound velocities measured at different propagation directions for 422 symmetry class crystals [12] and previously

TABLE I MATERIAL PARAMETERS OF ALN (SINGLE CRYSTALS AND THIN FILMS) AT ROOM TEMPERATURE

Material constant	Single crystal [Our results]	Thin film [1]	Thin film [2]	Thin film [3]	Single crystal [4]	Single crystal [5,6]	Single crystal [7]
C_{11} (GPa)	402.5	345	360	410	410.5		401.2
C_{12} (GPa)	135.6	125	122	140	148.5		135
C_{13} (GPa)	101	120	123	100	99		96.3±22.1
C_{33} (GPa)	387.6	395	410	390	388.5		368.2±27.9
C_{44} (GPa)	122.9	118	116	120	124.6	122	122.6
e_{33} (C/m^2)	1.34	1.55				1.39	1.84±0.71
e_{31} (C/m^2)	-0.6	-0.58				-0.57	-0.12±1.09
e_{15} (C/m^2)	-0.32	-0.48				-0.29	-0.26±0.03
$\varepsilon_{11}/\varepsilon_0$	9	8				8.5	
$\varepsilon_{33}/\varepsilon_0$	9.5	9.5				8.5	
ρ (kg/m^3)	3260	3260	3260		3255	3260	3260

determined density and dielectric constants. BAW velocity measurements on sample j) provide direct determination of the constants C_{11}, C_{33}, C_{44} and C_{66}. The remaining elastic constants C_{12} and C_{13} and piezoelectric stress constant e_{14} are sequentially determined using the measured sound velocities on specimens jj) and jjj) and known dielectric constant [12]. Temperature dependences of the elastic constants for $LiAlO_2$ single crystal at temperatures from 200 K to 310 K are summarized in Fig. 1.

dielectric constants almost linearly increase with temperature increasing. Obviously, such a behavior is typical of the ordinary linear dielectrics. Table II shows a full set of material parameters for $LiAlO_2$ single crystal at room temperature (T = 298 K). Notice that dielectric constants ε_{11} and ε_{33} as well as piezoelectric stress constant e_{14} for $LiAlO_2$ were measured for the first time. The results obtained give the opportunity to calculate first and second order temperature coefficients of

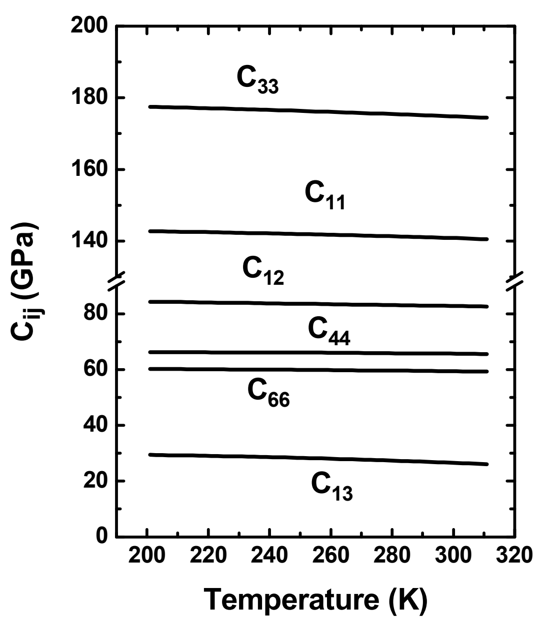

Figure 1. Temperature dependence of the elastic constants for $LiAlO_2$ single crystal

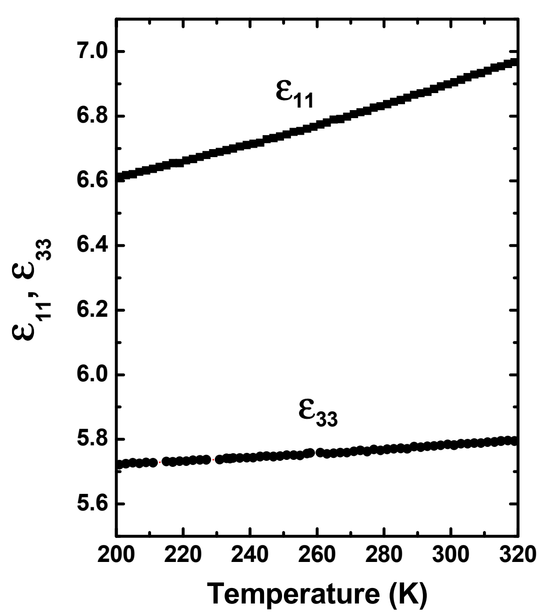

Figure 2. Temperature dependence of the relative dielectric constants ε_{11} and ε_{33} for $LiAlO_2$ single crystal

Temperature dependences of the dielectric constants ε_{11} and ε_{33} measured in the same temperature range as the elastic constants are presented in Fig. 2. As is seen from this figure,

material parameters (excluding e_{14}) which are also presented in Table II.

TABLE II MATERIAL PARAMETERS OF $LiAlO_2$ SINGLE CRYSTAL AND THEIR TEMPERATURE COEFFICIENTS

Material constant	Value at T = 298 K	First order TC, in 10^{-6} / K	Second order TC, in 10^{-9} / K^2
C_{11} (GPa)	141	-180.2	-497
C_{12} (GPa)	82.7	-194	-34
C_{13} (GPa)	27.9	-1362	-5270
C_{33} (GPa)	175	-190	-427
C_{44} (GPa)	65	-160	-337
C_{66} (GPa)	59.5	-182	-491
e_{14} (C/m^2)	0.16		
$\varepsilon_{11}/\varepsilon_0$	6.8	499	84.9
$\varepsilon_{33}/\varepsilon_0$	5.8	125	20.3
ρ (kg/m^3)	4650		

VI. CONCLUSION

High quality bulk AlN single crystal has been grown and its elastic, dielectric and piezoelectric properties have been evaluated. Material parameters show generally consistent results with previously published values for single crystalline samples. The piezoelectric constants e_{33} and e_{31} are somewhat different from those of the recently published set [7], and yet are in a good agreement with earlier results [5, 6] which may be due to both different crystals quality and diverse measurement techniques. A full set of the dielectric, elastic and piezoelectric constants for the commercially available $LiAlO_2$ single crystal has been obtained in a temperature range from 200 K to 310 K for the first time. Using the experimental data, temperature coefficients of material parameters (except e_{14}) of $LiAlO_2$ have been calculated.

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REFERENCES

[1] K. Tsubouchi, K. Sugai, N. Mikoshiba “AlN material constants evaluation and SAW properties on AlN/Al_2O_3 and AlN/Si”, IEEE Ultrason. Symp., pp. 375-380, 1981.

[2] G. Carlotti, F.S. Hickernell, H.M. Liaw, L. Palmieri, G. Socino, E. Verona “The elastic constants of sputtered aluminum nitride films”, Proc. IEEE Ultrason. Symp., pp. 353-356, 1995.

[3] C. Deger, E. Born, H. Angerer, O. Ambacher, M. Stutzmann, J. Hormsteiner, E. Riha, G. Fischerauer “Sound velocity of $Al_xGa_{1-x}N$ thin films obtained by surface acoustic wave neasurements”, Appl. Phys. Lett., vol. 72, pp. 2400-2402, 1998.

[4] L.E. McNeil, M. Grimsditch, R.H. French “Vibrational spectroscopy of aluminum nitride”, J. Amer. Ceram. Soc., vol. 76, pp. 1132-1136, 1993.

[5] G. Bu, D. Ciplys, M. Shur, L.J. Schowalter, S. Schujman, R. Gaska “Electromechanical coupling coefficient for surface acoustic waves in single-crystal bulk aluminum nitride”, Appl. Phys. Lett., vol. 84, pp. 4611-4613, 2004.

[6] G. Bu, D. Ciplys, M. Shur, L.J. Schowalter, S. Schujman, R. Gaska “Surface acoustic wave velocity in single-crystal AlN substrates”, IEEE Trans. UFFC, vol. 53, pp. 251-254, 2006.

[7] Y. Ohashi, M. Arakava, J.-ichi Kushibiki, B.M. Epelbaum, A. Winnacker “Ultrasonic microspectroscopy characterization of AlN single crystals”, Apll. Phys. Express, vol. 1, pp. 077004-1 – 077004-3, 2008.

[8] F. Jachmann, M. Pattabiraman, C. Hucho “Determination of the elastic moduli in $LiAlO_2$”, J. Appl. Phys., vol. 98, pp. 073501-1 - 073501-4, 1999.

[9] M.M.C. Chou, H.C. Huang, Y.F. Chang “Defects and acoustic properties of $LiAlO_2$”, Appl. Phys. Lett., vol. 88, pp. 161906-1 - 161906-3, 2006.

[10] S.V. Bogdanov “Acoustical method for the determination of the elastic and piezoelectric constants of crystals of classes 6mm and 4mm”, Acoust. Physics, vol. 46, pp. 530-533, 2000

[11] M. Onoe, H.F. Tiersten, A.H. Meitzler “Shift in the location of resonant frequencies caused by large electromechanical coupling in thickness-mode resonators”, J. Acoust. Soc. Amer., vol. 35, pp. 36-42, 1963.

[12] S.V. Bogdanov “Determination of the elastic and piezoelectric constants of crystals by an acoustical method”, Acoust. Physics, vol. 41, pp. 661-666, 1995.