View metadata, citation and similar papers at core.ac.uk

brought to you by CORE

東北大学機関リポジトリ
TOUR
Tohoku University Repository

Material Characterization of Piezoelectric Film and Frequency-Modulated Sensing Using Acoustic Wave Devices

著者	金子 亮介
number	63
学位授与機関	Tohoku University
学位授与番号	工博第5578号
URL	http://hdl.handle.net/10097/00127576

かね　こ　りょう　すけ
氏　　　　　名　金　子　亮　介
授　与　学　位　博士（工学）
学位授与年月日　平成３１年3月２７日
学位授与の根拠法規　学位規則第４条第１項
研究科，専攻の名称　東北大学大学院工学研究科（博士課程）ロボティクス専攻
学位論文題目　Material Characterization of Piezoelectric Film and Frequency-Modulated Sensing Using Acoustic Wave Devices（弾性波デバイスを用いた圧電薄膜の材料定数の評価と周波数変調センシング）
指　導　教　員　東北大学教授　田中　秀治
論文審査委員　主査　東北大学教授　田中　秀治　東北大学教授　小野　崇人
東北大学准教授　金森　義明　東北大学准教授　Joerg Froemel

論文内容要旨

High frequency piezoelectric MEMS resonator is a device using acoustic waves for sensing. So far, various types of these resonators have been developed for sensing because acoustic waves are sensitive to external perturbations, such as temperature, pressure, and so on. Such perturbations typically change the phase velocity of acoustic waves, resulting in a change of resonance frequency of resonators. Piezoelectric films (e.g. Aluminum nitride (AlN), Lead zirconate titanate (PZT), etc.) are commonly used for these resonators because they have advantages in terms of fabrication and mass-production.

In this thesis, the author proposes two questions as global motivations. The first question is whether there are any other new piezoelectric films for high frequency MEMS resonators. At present, PZT films are the most common material for piezoelectric MEMS because of its balanced performance. However, environmental compatibility of PZT is suspicious because it includes the Pb at high concentrations. Therefore, lead-free piezoelectric films have been important research target to replace PZT in piezoelectric MEMS. Among lead-free piezoelectric films, $CaTiO_3$-doped $(K,Na)NbO_3$ (KNN-CT) film is one of the promising candidates to replace PZT because it exhibit the highest level piezoelectric properties in lead-free piezoelectric films. Therefore, KNN-CT film can be an answer of this question. However, the full set of material constants (elastic constants, piezoelectric constants, dielectric constants) of the KNN-CT film, which are required for simulation of high frequency piezoelectric MEMS resonators, have not been revealed yet. In this study, therefore, the author investigated material constants of an as-deposited KNN-CT film and clarified the potential of the film as high frequency piezoelectric MEMS devices.

The second question as global motivations is whether other conventional piezoelectric materials can be extended in high frequency piezoelectric MEMS resonators for sensing applications. As for this question, the author focuses Polyvinylidene fluoride-trifluoroethylene (PVDF-TrFE), which is a well-known piezoelectric polymer, because its mechanical/electrical/ thermal properties are much different compared with inorganic materials. PVDF-TrFE are commonly used for MEMS because it has relatively high piezoelectric properties. In a first step of this study, the author developed a PVDF-TrFE-based film bulk acoustic resonator (FBAR).

After design, simulation and fabrication, the thickness expansion mode of FBARs are evaluated. Then, temperature and humidity sensing are done by frequency-modulation using the FBAR as a second step. The author clarified and discussed the potential of the PVDF-TrFE -based FBAR as high frequency piezoelectric MEMS devices.

The followings are the summary of chapters for the respective studies.

Chapter 2: Material Constant Extraction of $CaTiO_3$-doped $(K,Na)NbO_3$ Film using MEMS Resonators

In this chapter, the full set of material constants of an as-deposited KNN-CT film are investigated using MEMS-based resonators. In the case of piezoelectric bulk ceramics, a method to determine the full set of material constants is established as industrial standard (EMAS-6100). This method utilizes the following five piezoelectric resonators: length expander mode, radial expander mode, cylinder longitudinal mode, thickness longitudinal mode and thickness shear mode. The full set of material constants can be measured from resonance / anti-resonance frequency, electromechanical coupling coefficient (k^2) and the dimension of these resonators. However, these methods cannot be applied for c-axis oriented KNN-CT film because the cylinder longitudinal mode and the thickness shear mode resonators cannot be fabricated.

The author proposes a method with three steps to determine all the material constants of an as-deposited KNN-CT film on a 4 inch wafer. The first step is to measure a part of material constants using piezoelectric resonators which can be fabricated on a KNN-CT film. The piezoelectric resonators of length expander mode, radial expander mode and thickness longitudinal mode were fabricated with a KNN-CT-coated 4 inch wafer using MEMS technology. The full-coated Pt seed layer was utilized as the bottom electrodes of the resonators. XeF_2 etching was used to release the resonators at low temperature and low stress. As a result, $s_{11}^E = 9.27$ pm^2/N, $s_{12}^E = -3.06$ pm^2/N, $s_{66}^E = 24.7$ pm^2/N, $c_{33}^E = 89.8$ GPa, $d_{31} = -78.9$ pC/N, $\varepsilon_{33}^T/\varepsilon_0 = 1.27\times10^3$ were obtained.

The second step is to measure the phase velocities of leaky Lamb wave using an ultrasonic microscopy. The theoretical phase velocity of leaky Lamb wave is expressed using most of the material constants. Therefore, unknown constants can be determined by fitting measured phase velocities and theoretical ones. To obtain leaky Lamb wave, a self-suspended Al-metalized KNN-CT membrane was fabricated by MEMS technology. As a result, phase velocities of A_0 and S_0 modes of leaky Lamb wave were measured from 180 MHz to 270 MHz.

The third step is the numerical fitting of the measured and theoretical phase velocities. k_{33}, k_{15}, s_{13}^E, c_{44}^E and d_{15}, which are associated with cylinder thickness longitudinal mode and thickness shear mode, were extracted as fitting parameters. All of unknown constants can be calculated from the fitting parameters with the results of piezoelectric resonators. For such fitting, initial values of the fitting parameters are usually required, and they should be as close as the global solutions to avoid the risk of local convergence. However, material constants of non-doped KNN have to be used as initial values because few material constants of KNN-CT were reported, which increases the risk of local convergence with large error. Therefore, genetic algorithm is used for the fitting to overcome such local convergence problem. After the calculation of over 500 generations, the best solution was obtained when $k_{33} = 0.518$, $k_{15} =$

0.782, $s_{13}^E = -4.15$ pm^2/N, $c_{44}^E = 1.04$ GPa and $d_{15} = 1090$ pC/N. The full set of material constants of the KNN-CT film were then calculated from these parameters. The theoretical phase velocities with the calculated constants were in good agreement with the measured ones with the very small averaged error of 0.7% and 0.2% for A_0 and S_0 modes, respectively.

The determined material constants were reasonable compared to a hot-pressed bulk KNN. The extracted piezoelectric d and e constants were superior to that of AlN and ScAlN. The shear piezoelectric coefficient d_{15} is especially high, therefore the KNN-CT film has a potential for high frequency resonators using thickness shear mode. The extracted piezoelectric d and e constants were also competitive with PZT, which indicates the KNN-CT film has a potential to replace it. Although some of the determined constants may be affected by some errors, the full set of material constants of the KNN-CT film were successfully determined by the proposed method.

Chapter 3: Film Bulk Acoustic Resonator using PVDF-TrFE

In this chapter, a FBAR using a PVDF-TrFE film is developed and evaluated for the first time. The FBAR was designed as a membrane suspended by two anchors to be sensitive to external perturbations. Instead of pure PVDF-TrFE FBAR, a thermal SiO_2 film is added on the backside. Without the thermal SiO_2, stress is concentrated at the anchor parts due to large displacement during high voltage poling to obtain thickness expansion mode. The thermal SiO_2 layer is added to suppress the distortion. This structure is called PVDF-TrFE/SiO_2 composite in this study. Au electrode is used for the FBAR because it has good adhesion with PVDF-TrFE. When the FBAR is composed of 2 μm thick PVDF-TrFE film, 50 nm thick Au electrodes and 300 nm thick thermal SiO_2, resonance frequency is simulated as high as over 250 MHz. Note that material constants of a typical PVDF-TrFE are used for the simulation.

Next, the FBAR was fabricated on a SOI wafer using MEMS technology. PVDF-TrFE film was easily deposited by spin-coating and annealing. Because of low melting temperature of PVDF-TrFE (i.e. around 150°C), photolithography was done below 105°C. PVDF-TrFE was patterned by O_2 RIE. Top electrode was deposited by RF magnetron sputtering. XeF_2 etching was used to release the device. Process influence on PVDF-TrFE was evaluated for the O_2 RIE with a photoresist mask, Au sputtering and XeF_2 etching. The sputtering process influenced both surface morphology and crystal orientation of PVDF-TrFE. The RIE did not influence surface morphology, but it affect crystal orientation. The XeF_2 etching changes the morphology, but scarcely affect the crystal orientation.

After high voltage DC poling, thickness expansion mode was observed at 387.4 MHz with σ of 3.24 MHz regardless of the radius at 20°C. Because the SOI wafer is not for high frequency devices, de-embedding is conducted to compensate RF feed-through. The measured resonance frequency is much higher than the simulated one mainly because of the error of material constants of PVDF-TrFE. The impedance ratio and k^2 are 4.95–10.3 dB and 6.05–7.95%, respectively, when the radius of the device increases from 40 μm to 80 μm. Mechanical quality factor (Q_m) increases from 20 to 33 depending on the radius. Figure of merit (*FOM*) is also increases as the device size. The measured tan δ_e suggests that the PVDF-TrFE film is lossy compared with bulk one. Thickness expansion mode was characterized by a modified Butterworth-Van Dyke (MBVD) for a lossy piezoelectric transducer. As a result, dielectric loss is the most dominant loss, which is associate with the motion of electrons in high frequency. The low Q_m is derived from the dielectric loss.

Chapter 4: Sensing Applications of PVDF-TrFE/SiO$_2$ Composite FBAR

In this chapter, temperature and humidity sensing are conducted using a PVDF-TrFE/SiO$_2$ composite FBAR. For the sensing experiment, a FBAR of 80 μm radius was connected to a SMA connector mounted on a FR-4 substrate. Ag paste was used to connect Cu wires with electrodes. After the implementation, the Allan variance of FBAR was 1.0 ppm at an averaging time of 1.0 s. White FM noise is dominant when the averaging time is less than 0.1 s, while random walk noise was dominant when the averaging time is over 0.1 s.

Next, temperature sensitivity was measured for both ramping up (from 25°C to 80°C) and ramping down processes (from 14°C to 6°C). As a result, temperature sensitivity was as large as -0.384 MHz/°C (i.e. -1029 ppm/K) for ramping up and -0.639 MHz/°C (i.e. -1679 ppm/K) for ramping down. Temperature hysteresis of resonance frequency was less than 1% in average for both process. Resonance frequency, Q_m and *FOM* are continuously increased as the measurement temperature decreases, which suggests the sensor performance is improved by cooling. Then, MBVD model was used to characterize the temperature dependency. As a result, mechanical losses such as anchor loss and viscoelasticity loss become low at low temperature region. Dielectric property of PVDF-TrFE decreases by cooling. However, it was also observed that the sensing performance drastically deteriorated when condensation occurred on PVDF-TrFE at low temperature region. Condensation also causes significant hysteresis of resonance frequency because of the characteristic change of PVDF-TrFE. Therefore, it is necessary to use the FBAR in a dry condition.

Next, humidity sensitivity was measured by changing relative humidity (RH) from 5% to 89%. When it is less than 50% RH, resonance frequency was almost constant. Resonance frequency gradually decreased when RH increases from 50% to 89%, but the sensitivity was as small as -0.012 MHz/RH% (i.e. -32 ppm/RH%). In addition, hysteresis occurred because of condensation. Therefore, it is not suitable to use the FBAR as a humidity sensor.

Actually, the accuracy of sensing data using the PVDF-TrFE/SiO$_2$ composite FBAR is not so good because of the low Q. The Q must be improved by increasing crystallinity of PVDF-TrFE, decreasing damage induced by fabrication process, and so on. The Q also will be improved by making the membrane part of the FBAR large. It is also an option to conduct the sensing at low temperature region to increase Q. In this way, the PVDF-TrFE/SiO$_2$ composite FBAR will be useful for temperature (or low temperature) sensors.

As general conclusion, the potentials of the KNN-CT film and the PVDF-TrFE for high frequency piezoelectric MEMS devices are clarified in this thesis. The obtained results in each chapter provides new perspectives of these materials. With further improvements of the films and resonators, it is promising to obtain new high frequency piezoelectric MEMS resonators using these films.

論文審査結果の要旨

圧電高周波共振子は，MEMS の基本的な構成要素の 1 つである。従来，これには圧電材料として AlN や ZnO の薄膜が多用されてきた。しかし，他にも多様な圧電材料があり，その中には AlN や ZnO と比べて特徴的な材料特性を示すものもある。したがって，従来，高周波 MEMS 共振子に用いられてこなかった圧電薄膜の可能性を検討することは，MEMS の新たな応用を広げるためにも重要である。

本論文は，非鉛強誘電体圧電材料である CaTiO3 ドープ(K,Na)NbO3（KNN-CT），および高分子圧電材料であるポリフッ化ビニリデン・三フッ化エチレン共重合体（PVDF-TrFE）を選び，その高周波 MEMS 共振子への適用可能性を，材料特性，微細加工性，共振性能，センシング応用性などの観点から研究した一連の成果をまとめたものであり，全編 5 章からなる。

第 1 章は序論であり，研究の背景として従来の圧電 MEMS 共振子が説明された後，KNN-CT と PVDF-TrFE に関する従来の研究が概観されている。

第 2 章では，高周波 MEMS 共振子を用いた KNN-CT の材料定数評価法について述べている。圧電 MEMS を設計するにあたり，利用する圧電薄膜の材料定数を知ることは必須である。しかし，バルク材料と異なり，薄膜の圧電材料の圧電定数，弾性定数，および誘電率を全て決めることは容易ではない。ここでは，2 段階の方法を用いてこれを行っている。まず，KNN-CT 薄膜を用いて複数種の高周波 MEMS 共振子を作製し，それを評価することで材料定数の一部を決定する。次に，収束超音波顕微鏡を用いて，自己支持された KNN-CT 薄膜を伝わる音響波の音速を計測し，一方，第一段階で得た材料定数と未知であるが仮定した材料定数を理論モデルに当てはめて理論音速を計算し，両者が一致するように遺伝的アルゴリズムを用いて未知の材料定数を決定する。この方法によって，KNN-CT の材料定数を全て決定している。これは，圧電薄膜の新しい材料評価法として有用かつ重要な成果である。

第 3 章では，PVDF-TrFE を用いた薄膜バルク音響共振子（Film Bulk Acoustic Resonator，FBAR）を設計，試作，および評価した結果が報告されている。高周波フィルタに多用されている FBAR はセンサとしても有望であるが，その圧電層を無機材料と比べて桁違いに柔らかい有機材料の PVDF-TrFE にすることによって，センサの高感度化，あるいは新たなセンサへの応用が可能になると期待される。有限要素法を用いて PVDF-TrFE FBAR が設計され，また，高温や溶媒に弱いという PVDF-TrFE の材料特性を考慮した作製プロセスが開発されている。その結果，数百 MHz 帯の FBAR が試作され，周波数特性が評価されている。これは，PVDF-TrFE を用いた高周波 FBAR を総合的に研究した最初の成果であり，重要な知見である。

第 4 章では，PVDF-TrFE FBAR のセンシング応用を目指し，その発振周波数安定性，温度特性，および湿度応答性を調べた結果が報告されている。PVDF-TrFE FBAR の温度特性が高温から低温にわたって実測され，周波数の温度依存性が大きいことが見出されている。これを踏まえ，PVDF-TrFE FBAR の温度センサまたは赤外線センサとしての可能性が議論されている。次に，湿度に対する周波数とインピーダンスの変化が実測されている。PVDF-TrFE FBAR は湿度感受性を有するものの，低湿度領域では感度が低く，また，再現性の問題もあることが明らかにされている。これは，PVDF-TrFE FBAR の外部刺激への応答性を調べた最初の結果であり，重要な知見である。

第 5 章は結論である。

以上要するに本論文は，高周波 MEMS 共振子の新しい圧電薄膜として，KNN-CT と PVDF-TrFE に着目し，材料評価，デバイス試作，デバイス評価から応用可能性までを総合的に研究して，新たな知見を得た成果をまとめたものであり，ロボティクス，およびスマートシステム集積学に寄与するところが少なくない。

よって，本論文は博士(工学)の学位論文として合格と認める。