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主　論　文　の　要　旨

論文題目　**Study on Nanostructured $Pb(Zr,Ti)O_3$ for Piezoelectric Energy Harvesting**
(圧電エナジーハーベスティングに資する $Pb(Zr,Ti)O_3$ のナノ構造化に関する研究)

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論　文　内　容　の　要　旨

Piezoelectric materials are the materials whose polarization changes when we applied force on them. The application of piezoelectric materials is various, among which piezoelectric energy harvesting (PEH) is one of the most popular ones, due to the efficient and rapid conversion from mechanical energy in the environment to electric power. The output power of PEH devices can be simply evaluated by the available energy, which is determined by the figure of merit (FOM), induced stress and volume. In general, the induced stress can easily be increased by optimizing the device configuration, but improving the FOM, which is determined by the material property, would need more costs and efforts.

There are some problems in enhancing FOM, especially for the microscale or even nanoscale PEH devices. For the traditional piezoelectric bulks or thick films, a giant piezoelectric constant can be achieved with the composition near morphotropic phase boundary (MPB), but for the thin films, it has been reported that the piezoelectric property is significantly affected by the substrate clamping. In addition, within a limited volume, it would be difficult to construct a PEH optimized for a frequency lower than 100 Hz using a conventional cantilever beam structure. Such problems are due to the small size of the thin films. The electric and electromechanical properties are affected by many factors, not only including temperature and composition that mainly affect the bulks, but also the internal stress, thickness and electrostatic boundary, etc. Among these factors, it is interesting to pay attention to the effect of internal stress. On one hand, it is easy to think of the strategy to eliminate the stress so the demerit of the substrate clamping can be avoided. On the other hand, it may also be possible to utilize the stress to improve the property in a positive way.

In this study, methods and analyses on the improvement of piezoelectric response and output performance for the highly-oriented ferroelectric thin films are based on these two perspectives, and two objectives are established as follows. (1) Fabricating and evaluating aligned PZT nanorods to improve the output performance, from the perspective of reducing the lateral stress (Chapter 2 – Chapter 4). (2) Fabricating and evaluating PZT superlattice films to improve the piezoelectric response, from the perspective of utilizing the lateral stress (Chapter 5 – Chapter 6). The contents of each chapter are explained in detail as follows.

Chapter 2 – Theoretical analysis on the output performance of piezoelectric nanorod arrays

From the perspective of reducing the clamping stress in the film, using the piezoelectric nanorod array would be an effective way to improve the output performance along the out-of-plane direction. In this chapter, a theoretical model of a nanorod array is studied on the output voltage and power, by deducing their expressions from the piezoelectric equations and conducting the FEM simulation in the software *COMSOL Multiphysics*. It is shown that a low lateral stress is induced in the piezoelectric unit with a large aspect ratio, indicating the easier deformation of the nanorods than that of the film when the same stress is applied. d_{33} of the nanorods is closed to the bulk d_{33} which is 33% higher than the clamped direct d_{33} for the film, and thus a 77% enhanced FOM_{33}. And the density of the nanorod array could achieve larger V_{open} and P_{out} than those of a dense film, showing a larger impact over the aspect ratio. The conventional cantilever achieves large input power at resonance due to a low spring constant, while the 33-mode nanorod array structure show the P_{out}/P_{in} twice higher than that of the 31-mode film cantilever structure, indicating the promising application of the off-resonant nanorod arrays.

Chapter 3 – Enhanced FOM from the decreased density of PZT nanorod arrays

The theoretical study has predicted the enhanced output power of using the nanorod array, due to the increased d_{33} and the decreased density compared with a 33-mode film. It is worth noting that the decreased density achieved in the nanorod array is significant to improve FOM for the PEH application since there is seldom a straightforward way to achieve a high FOM in a piezoelectric film due to the positive correlation between dielectric and piezoelectric properties. This study experimentally clarified that the effective FOM of the PZT nanorod array can be enhanced by the decreased density by comparing the nanorods with a film having the same orientation and similar domain structure. This approach enables us to independently control the piezoelectric and dielectric constants of materials, making it possible to lower the effective dielectric constant while maintaining the piezoelectric constant. In addition, a method to distinguishes the effect of the decreased density from that of the other factors is proposed, which makes it possible to evaluate the FOM of the nanorod array in a more accurate way.

Chapter 4 – Fabrication of PZT nanorods by RF-magnetron sputtering

For the purpose of commercializing the nanorod-based PEH devices, PZT nanorods are expected to grow in an area up to several cm^2 and thus the fabrication using RF-magnetron sputtering is taken into consideration. In this chapter, the strategy to grow PZT nanorods by RF-magnetron sputtering and the optimal fabrication condition are investigated. It is shown that the effect of the O_2 partial pressure plays a considerable important role in growing PZT nanorods, which makes it possible to achieve the nanorod structure at low pressure, and thus the rapid growth can be the dominant factor to grow the nanorods by adjusting $Ar{:}O_2$. Finally, a nanorod-like PZT is obtained with $Ar{:}O_2 = 2{:}1$ at 650 °C, even though using a general working pressure of 2.7 Pa. The possibility to achieve nanorods would be enhanced by further increasing the growth rate of sputtering.

Chapter 5 – Theoretical analysis on piezoelectric response of ferroelectric superlattice films

Previous studies have revealed the possibility of improving the piezoelectric response by utilizing the lateral stress. However, it is difficult to validate this possibility in a single-layer film with a thickness over 100 nm, in which a multidomain structure will form due to the local deformation determined by the minimal elastic energy. The possibility of utilizing the lateral stress to control the polarization rotation is predicted with the Landau theory, with respect to the single-domain structure in the single-layer film and the superlattice film. u_m-E_{ext} phase diagrams of the single-layer films confirm this possibility, and detailed analyses on the stabilized polarization, dielectric and piezoelectric properties of the (111)-oriented superlattice films reveal the potential of exhibiting enhanced piezoelectric response. It is shown that a unique polarization state known as *aac* phase is stabilized in the single-domain films, different from the polarization in bulks. When the external electric field is applied, discontinuity of the polarization extension, dielectric constant and piezoelectric constant are observed at *aac-r* phase transition boundary. It is worth noting that improved piezoelectric response that exceeds the clamped bulks and is comparable to the free bulks is observed by utilizing the lateral stress in the films.

Chapter 6 – Larger piezoelectric response from polarization rotation in artificial superlattice films

The theoretical analysis has predicted an enhanced piezoelectric property by achieving a desired misfit strain to induce the polarization rotation in a single-domain film. The prediction can be validated by fabricating the superlattice films. In this chapter, (111)-epitaxial artificial superlattice films consisting of $Pb(Zr_{0.4}Ti_{0.6})O_3$ and $Pb(Zr_{0.6}Ti_{0.4})O_3$ were fabricated by PLD, which is in accordance with the theoretical model. From the characterization of XRD and STEM, the multidomain structure forms in the film with the thickness over 12 nm but the single-domain structure forms in that with 3 nm thickness. The superlattice structure can serve as an effective strategy for utilizing the lateral stress in the films with the thickness over 100 nm. For the superlattice film with 3 nm thickness, a tilted polarization direction is characterized, agreeing with the *aac*-phase in the theoretical study. This polarization state is different from that in the PZT bulks and indicates the polarization rotation which would improve the piezoelectric response. The piezoelectric constant d_{33} of 66 pm/V is achieved, higher than the clamped PZT bulks as well as the multidomain films with the layer thickness over 12 nm. The enhancement agrees with the theoretical analysis. It is considered that the polarization state of the *aac* phase would be susceptible to the external electric field and generate the polarization rotation easily.

In conclusion, the strategy to improve the piezoelectric property and the output power for the application of PEH devices focused on how to deal with the internal stress of the PZT layers, and the two types of nanostructure, nanorod array and artificial superlattice, were analyzed theoretically and proved effective by experiments. The nanorod array showed a larger effective FOM than the clamped films in the 33 mode, due to the large aspect ratio of the PZT units and reduced density of the PEH device. The effect of the decreased density was also clarified by direct experiments, and a method to distinguish this effect from other factors was also proposed. The superlattice structure was proved effective to achieve a piezoelectric property over the bulks by utilizing the lateral stress. The fully clamped single-domain films exhibited a unique polarization state which is susceptible to the external electric field, indicating a large field-induced strain by the polarization rotation.