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Three-Scale Structure Analysis Code and Thin Film Generation of a New Biocompatible Piezoelectric Material MgSiO₃

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1. Introduction

In this study, three subjects were investigated for a new biocompatible piezoelectric material generation:
1. Development of a numerical analysis scheme of a three-scale structure analysis and a process crystallographic simulation.
2. Design of new biocompatible piezoelectric materials.
3. Generation of MgSiO₃ thin film by using radio-frequency (RF) magnetron sputtering system.

Until now, lead zirconate titanate (Pb(Zr,Ti)O₃: PZT) has been used widely for sensors (Hindrichsen et al., 2010), actuators (Koh et al., 2010), memory devices (Zhang et al., 2009) and micro electro mechanical systems (MEMS) (Ma et al., 2010), because of its high piezoelectric and dielectric properties. The piezoelectric thin film with aligned crystallographic orientation shows the highest piezoelectric property than any polycrystalline materials with random orientations. Sputtering (Bose et al., 2010), chemical or physical vapor deposition (CVD or PVD) (Tohma et al., 2002), pulsed laser deposition (PLD) (Kim et al., 2006) and molecular beam epitaxy (MBE) (Avrutin et al., 2009) are commonly used to generate high performance piezoelectric thin films. Lattice parameters and crystallographic orientations of epitaxially grown thin films on various substrates can be controlled by these procedures. K. Nishida et al. (Nishida et al., 2005) generated [001] and [100]-orientated PZT thin films on MgO(001) substrate by using CVD method. They succeeded to obtain a huge strain caused by the two effect: the synergetic effect of [001] orientation with the piezoelectric strain; and the strain effect of [100] orientation caused by switching under conditions of the external electric field. Additionally, PZT-based piezoelectric materials, such as Pb(Zn₁/₃Nb₂/₃)O₃-PbTiO₃ (Geetika & Umarji, 2010) and PbMg₁/₃Nb₂/₃O₃-PbTiO₃ (Kim et al., 2010), have also been developed.

However, lead, which is a component of PZT-based piezoelectric material, is the toxic material. The usage of lead and toxic materials is prohibited by the waste electrical and electronic equipment (WEEE) and the restriction on hazardous substances (RoHS).

For alternative piezoelectric materials of the PZT, lead-free piezoelectric materials have been studied. J. Zhu et al. (Zhu et al., 2006) generated [111]-orientated BaTiO₃ on LaNiO₃(111) substrate, which had a crystallographic orientation with maximum piezoelectric strain.
constants. S. Zhang et al. (Zhang et al., 2009) doped Ca and Zr in BaTiO$_3$ and succeeded in generating the piezoelectric material with high piezoelectric properties. Further, P. Fu et al. (Fu et al., 2010) doped La$_2$O$_3$ in Bi-based $(Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}TiO_3$ and succeeded in generating a high performance piezoelectric material. However, their goals were to develop an environmentally compatible piezoelectric material, and the biocompatibility of their piezoelectric materials has not been investigated. Therefore, their piezoelectric materials could not be applied for Bio-MEMS devices.

Recently, the Bio-MEMS, which can be applied to the health monitoring system and the drug delivery system, is one of most attractive research subject in the development of the nano- and bio-technology. Therefore, the biocompatible actuator for the micro fluidic pump in Bio-MEMS is strongly required. However, they remain many difficulties to design new biocompatible materials and find an optimum generation process. Especially, it is difficult to optimize the thin film generation process because there are so many process factors, such as the substrate material, the substrate temperature during the sputtering, the target material and the pressure in a chamber. Therefore, the numerical analysis scheme is necessary to design new materials and optimize the generation process.

The analysis scheme based on continuum theory is strongly required, due to time consuming experimental approach such as finding an optimum sputtering process and a substrate crystal structure through enormous experimental trials. The analysis scheme should predict the thin film deformation, strain and stress, which are affected by the imposed electric field and are constrained by the substrate.

Until now, the conventional analysis schemes, such as the molecular dynamics (MD) method (Rubio et al, 2003) and the first-principles calculation based on the density functional theory (DFT) (Lee & Chung, 2006), have been applied to the crystal growth process simulations. The MD method has been used mainly to analyze the crystal growth process of pure atoms. J. Xu et al. (Xu & Feng, 2002) calculated the Ge growth on Si(111). In the cases of the perovskite compounds, the MD method has been applied to analyze the phase transition, the polarization switching and properties of crystal depending on temperature and pressure. J. Paul et al. (Paul et al., 2007) analyzed the phase transition of BaTiO$_3$ caused by rising temperature and S. Costa et al. (Costa et al., 2006) analyzed the one of PbTiO$_3$ caused by rising temperature and pressure. However, the reliability of its numerical results is poor due to its uncertain inter-atomic potentials for the various combinations of atoms. The MD method could not predict the differences of poly-crystal structures and material properties caused by changing combinations of the crystals and the substrates. It can be concluded that the conventional MD method has many problems for the crystal growth prediction of perovskite compounds grown on the arbitrarily selected substrates.

On the other hand, the DFT can treat interactions between electrons and protons, therefore the reliable inter-atomic potentials can be obtained. The first-principles calculations based on the DFT were applied to the epitaxial growth of the ferroelectric material by O. Dieguez et al. and I. Yakovkin et al.. O. Dieguez et al. (Dieguez et al., 2005) evaluated the stress increase and the polarization change caused by the lattice mismatch between a substrate and a thin film crystal, such as BaTiO$_3$ and PbTiO$_3$. Similarly, I. Yakovkin et al. (Yakovkin & Gutowski, 2004) has investigated in the case of SrTiO$_3$ thin film growth on Si substrate. However, these analyses adopted limited assumptions, such as fixing the conformations of thin film crystals and the growth orientations on the substrates. In this conventional algorithm, the grown orientation is determined by the purely geometrical lattice mismatch.
between thin films and substrates. This algorithm is not sufficient to predict accurately the
preferred orientation of the thin film.
In order to generate the new piezoelectric thin film, a crystal growth process of the thin film
should be predicted accurately. The stable crystal cluster of the thin film, which consists
geofometrically with substrate crystal, is grown on the substrate. Generally, the crystal cluster
is an aggregate of thin film crystals. Their morphology and orientations were varied
according to the combination of the thin film and the substrate crystals. Therefore, the
numerical analysis scheme of the crystal growth process, which can find the best
combination of the thin film and the substrate crystal, is strongly required, to optimize the
new piezoelectric thin film.
In this chapter, following contents are discussed to develop the new biocompatible MgSiO₃
piezoelectric thin film.
1. The three-scale structure analysis algorithm, which can design new piezoelectric
materials, is developed.
2. The best substrate of the MgSiO₃ piezoelectric thin film is found by using the three-scale
structure analysis code.
3. The MgSiO₃ thin film is grown on the best substrate by using the RF magnetron
sputtering system, and piezoelectric properties are measured.
4. An optimum generating condition of the MgSiO₃ piezoelectric thin film is found by
using the response surface method.
Section 2 provides the description to the algorithm of the three-scale structure analysis code
on basis of the first-principles calculation, the process crystallographic simulation and the
crystallographic homogenization theory. Section 3 provides the best substrate of the new
biocompatible MgSiO₃ piezoelectric thin film calculated by the three-scale structure analysis
code. In section 4, the optimum generating condition of MgSiO₃ piezoelectric thin film is
found. Finally, conclusions are given in section 5.

2. A three-scale structure analysis code

This section describes the physical and mathematical modelling of the three-scale structure
and the numerical analysis scheme of three-scale structure analysis to characterize and
design epitaxially grown piezoelectric thin films. The existing two-scale finite element
analysis is the effective analysis tool for characterization of existing piezoelectric materials.
This is because virtually or experimentally determined crystal orientations can be employed
for calculation of piezoelectric properties of the macro continuum structure (Jayachandran et
al., 2009). However, it can not be applied to a new piezoelectric material, due to unknown
crystal structure and material properties.
Figure 1 shows the schematic description of the three-scale modelling of a new piezoelectric
thin film, which is grown on a substrate. It shows the three-scale structures, such as a
“crystal structure”, a “micro polycrystalline structure” and a “macro continuum structure”.
In the crystal structure analysis, stable structures and crystal properties are evaluated by
using the first-principles calculation. Preferred orientations and their fraction are calculated
by using the process crystallographic simulation in the micro polycrystalline structure
analysis. The macro continuum structure analysis provides the piezoelectric properties of
the thin film by using the finite element analysis on basis of the crystallographic
homogenization theory. Therefore, the three-scale structure analysis can predict the epitaxial
growth process of not only the existent piezoelectric materials but also the new ones.

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2.1 Crystal structure analysis by using the first-principles calculation
2.1.1 Stable crystal structure analysis
The stable structures of the perovskite cubic are calculated by the first-principles calculation based on the density functional theory (DFT) by using the CASTEP code (Segal et al., 2002). The stable structures are, then, computed using an ultra-soft pseudo potential method under the local density approximation (LDA) for exchange and correlation terms. A plane-wave basis set with 500eV cutoff energy is used and special k-points are generated by an 8x8x8 Monkhorst-pack mesh (Monkhorst et al., 1976).

The perovskite-type compounds ABX₃ provide well-known examples of displacive phase transitions. They are in a paraelectric non-polar phase at high temperature and have a cubic crystal structure (lattice constant a = c). The cubic crystal structure consists of A cations in the large eightfold coordinated site, B cations in the octahedrally coordinated site, and X anions at equipoint. The stability of cubic crystal structure can be estimated by an essential geometric condition, tolerance factor t. If ion radiiuses of A, B and X are indicated with rₐ, rₜ, rₓ, tolerance factor t can be described as

\[ t = \frac{r_a + r_x}{\sqrt{2} (r_B + r_x)} \]

When tolerance factor t consists in the range from 0.75 to 1.10, the perovskite-type crystal structure has high stability. The cubic crystal structure often distorts to ferroelectric phase of lower symmetry at decreased temperature, which is a tetragonal crystal structure (a > c) with spontaneous polarization. These ferroelectric distortions are caused by a soft-mode of phonon vibration in cubic crystal structure, and it brings to good piezoelectricity. The soft-mode can be distinguished from other phonon vibration modes with negative eigenfrequency, and the transitional crystal structure depends strongly on the eigenvectors. Consequently, new biocompatible piezoelectric materials are searched according to the flowchart in Fig. 2. Firstly, biocompatible elements are inputed to A and B cations while halogens and chalcogens are set to X anion for the perovskite-type compounds. The combination of three elements is determined to satisfy the stable condition of the tolerance factor. The stable cubic structure of perovskite-type oxides is calculated to minimize the
total energy. Next, the phonon vibration in the stable cubic structure is analyzed to catch the soft-mode which causes a phase transition from the paraelectric non-polar phase (cubic structure) to the ferroelectric phase (tetragonal structure). When the eigenfrequency of phonon vibration is positive, it is considered that the cubic structure is the most stable phase and does not change to other phase. On the other hand, in case that the eigenfrequency is negative, the cubic structure is guessed to be an unstable phase and change to other phase corresponding to the soft-mode. Additionally, if all eigenvectors of constituent atoms are parallel to $c$ direction in crystallographic coordinate system, it is supposed to change from cubic to tetragonal structure. If not, it is supposed to transit to other structures except tetragonal one. On the base of phonon properties, the stable tetragonal structure with minimum total energy is searched using the eigenvector components for the initial atomic coordinates.

Fig. 2. The flowchart of searching new piezoelectric materials by the first-principles DFT.
Recently, many perovskite cubic crystals such as SrTiO$_3$ and LaNiO$_3$ have been reported. However, most of these materials could not be transformed into a tetragonal structure below Curie temperature, because most of perovskite cubic crystals are more stable than tetragonal crystals. Therefore, the tetragonal structure indicates a soft-mode of the phonon oscillation in cubic structure. Lattice parameters and piezoelectric constants of the tetragonal structure are calculated using the DFT.

2.1.2 Characterization of piezoelectric constants

The total closed circuit (zero field) macroscopic polarization of a strained crystal $P^T_i$ can be described as,

$$P^T_i = P^S_i + e_{ii} \varepsilon,$$

where $P^S_i$ is the spontaneous polarization of the unstrained crystal (Szabo et al., 1998, 1999). Under Curie temperature, ferroelectric crystal with tetragonal structure has a polarization along the $c$ axis. The three independent piezoelectric stress tensor components are $e_{31} = e_{23}$, $e_{15} = e_{24}$, $e_{33}$ and $e_{15}$ describe the zero field polarization induced along the $c$ axis, when the crystal is uniformly strained in the basal $a$-$b$ plane or along the $c$ axis, respectively. $e_{15}$ measures the change of polarization perpendicular to the $c$ axis induced by the shear strain. This latter component is related to induced polarization by $P_1 = e_{15} \varepsilon_5$ and $P_2 = e_{15} \varepsilon_4$.

The total induced polarization along $c$ axis can be described by a sum of two contributions.

$$P^i_3 = e_{33} \varepsilon_3 + e_{31} \left( \varepsilon_1 + \varepsilon_2 \right)$$

where $\varepsilon_1 = (a - a_0)/a_0$, $\varepsilon_2 = (b - b_0)/b_0$ and $\varepsilon_3 = (c - c_0)/c_0$ are strains along the $a$, $b$ and $c$ axes, respectively, and $a_0$, $b_0$ and $c_0$ are lattice parameters of the unstrained structure.

The electronic part of the polarization is determined using the Berry’s phase approach (Smith & Vandelbilt, 1993), a quantum mechanical theorem dealing with a system coupled under the condition of slowly changing environment. One can calculate the polarization difference between two states of the same solid, under the necessary condition that the crystal remains an insulator along the path, which transforms the two states into each other through an adiabatic variation of a crystal Hamiltonian parameter $\lambda_H$. The magnitude of the electronic polarization of a system in state $\lambda_H$ is defined only modulo $e\Omega/R$, where $R$ is a real-space lattice vector, $\Omega$ the volume of the unit cell, and $e$ the charge of electron. In practice, the $e\Omega/R$ factor can be eliminated by careful inspection, in the condition where the changes in polarization are described as $|\Delta P| \ll |e\Omega/R|$. The electronic polarization can be described as,

$$P^e(\lambda_H) = \frac{2e}{(2\pi)^3} \int_{\text{BZ}} d\mathbf{k} \frac{\partial}{\partial k} \psi_{\lambda_H}(\mathbf{k},\mathbf{k}') \bigg|_{\mathbf{k} = \mathbf{-k}}$$

where the integration domain is the reciprocal unit cell of the solid in state $\lambda_H$ and $\psi_{\lambda_H}$ is quantum phase defined as phases of overlap-matrix determinants constructed from periodic parts of occupied valence Bloch states $\nu_{\nu}^{\lambda_H}(\mathbf{k})$ evaluated on a dense mesh of $\mathbf{k}$ points from $\mathbf{k}_0$ to $\mathbf{k}_0 + b$, where $b$ is the reciprocal lattice vector.
The electronic polarization difference between two crystal states can be described as,

$$\Delta P^{el} = P^{el}(\lambda_{H2}) - P^{el}(\lambda_{H1})$$  \hspace{1cm} (6)$$

Common origins to determine electronic and core parts are arbitrarily assigned along the crystallographic axes. The individual terms in the sum depend on the choice, however, the final results are independent of the origins.

The elements of the piezoelectric stress tensor can be separated into two parts, which are a clamped-ion or homogeneous strain $u$, and a term that is due to an internal strain such as relative displacements of differently charged sublattices

$$e_{iv} = \frac{\partial P_T^{T}}{\partial \epsilon_v} + \sum_k \frac{\partial P_T^{T}}{\partial u_{k,i}}$$ \hspace{1cm} (7)$$

where $P_T^{T}$ is the total induced polarization along the $i$th axis of the unit cell.

Equation (7) can be rewritten in terms of the clamped-ion part and the diagonal elements of Born effective charge tensor.

$$e_{iv} = e^{(0)}_{iv} + \sum_k \frac{e_a T_{k,ii}^{*}}{\Omega} \frac{\partial u_{k,i}}{\partial \epsilon_v}$$ \hspace{1cm} (8)$$

where $\phi$ is the lattice parameter, the clamped-ion term $e^{(0)}$ is the first term of Eq. (8). $e^{(0)}$ is equal to the sum of rigid core $e^{(0)}$, core and valence electronic $e^{(0)el}$ contributions. Subscript $k$ corresponds to the atomic sublattices. $Z^{*}$ is the Born effective charge described as,

$$Z_{k,iv}^{*} = Z_{k,iv}^{core} + e_{iv}^{(0)} = \frac{\Omega}{e_a} \frac{\partial P^{T}}{\partial \epsilon_v}$$ \hspace{1cm} (9)$$

Piezoelectric response includes two contributions, that appear in linear response for finite distortional wave vectors $q$, and contributions which appear at $q = 0$. Improper polarization changes arise from the rotation or dilation of the spontaneous polarization $P_s$. The proper polarization of a ferroelectric or pyroelectric material is given by

$$P^{p}_{ij} = P^{T}_{ij} - \sum_j \left( e_{ij} P_{j}^{T} - e_{ij}^{(0)} P_{j}^{s} \right)$$ \hspace{1cm} (10)$$

Proper piezoelectric constants $e^{p}_{ij}$ can be described as,

$$e^{p}_{11} = \frac{\partial P_{1}^{T}}{\partial \epsilon_1} + P_{3}^{s}$$ \hspace{1cm} (11)$$

$$e^{p}_{15} = \frac{\partial P_{1}^{T}}{\partial \epsilon_5} - P_{3}^{s}$$ \hspace{1cm} (12)$$
and $e_{31}^{P} = e_{31}^{T}$, because the improper part of $e_{33}^{T}$ is zero. The difference between proper polarization and total one is due to only homogeneous part, which can be described in the following equation for $e_{31}$ ($e_{31}^{P,\text{hom}}$).

$$e_{31}^{P,\text{hom}} = e_{31}^{\text{hom}} + P_{3}^{\text{el}} = \frac{\varepsilon_{31}^{el,T}}{\varepsilon_{31}} + P_{3}^{\text{el,s}}$$ (13)

This equation can use the similar expression for $e_{15}^{P,\text{hom}}$. The homogeneous part appears as a pure electronic term in the expression for the proper piezoelectric constants, which differ in crystal with nonzero polarization in the unstrained state. The first term in Eq. (8) can be evaluated by polarization differences as a function of strain, with the internal parameters kept fixed at their values corresponding to zero strain. The second term, which arises from internal microscopic relaxation, can be calculated after determining the elements of the dynamical transverse charge tensors and variations of internal coordinate $u_{i}$ as a function of strain. Generally, transverse charges are mixed second derivatives of a suitable thermodynamic potential with respect to atomic displacements and electric field. They evaluate the change in polarization induced by unit displacement of a given atom at the zero electric field to linear order. In a polar insulator, transverse charges indicate polarization increase induced by relative sublattice displacement. While many ionic oxides have Born effective charges close to their static value, ferroelectric materials with perovskite structure display anomalously large dynamical charges.

2.2 Micro polycrystalline structure analysis by using the process crystallographic simulation

2.2.1 Evaluation method of the total energy

The tetragonal crystal structure of perovskite compound and its five typical orientations [001], [100], [110], [101] and [111] are shown in Fig. 3. Considering a epitaxial growth of the crystal on a substrate, the lattice constants including $a$, $b$, $c$, $\theta_{ab}$, $\theta_{bc}$ and $\theta_{ca}$ are changed because of the lattice mismatch with the substrate. These crystal structure changes can be determined by considering six components of mechanical strain in crystallographic coordinate system such as $\varepsilon_{aa}$, $\varepsilon_{bb}$, $\varepsilon_{cc}$, $\gamma_{ab}$, $\gamma_{bc}$ and $\gamma_{ca}$. In a general analysis procedure, the lattice mismatch in the specific direction was calculated and the crystal growth potential was derived. However, the epitaxially grown thin film crystal is in a multi-axial state. Therefore, the numerical results of the crystal energy of thin films are not corrected when considering only uni-axis strain. In this study, the total energy of a crystal thin film with multi-axial crystal strain states is calculated by using the first-principles calculation, and is applied to the case of the epitaxial growth process. An ultra-soft pseudo-potentials method is employed in the DFT with the condition of the LDA for exchange and correlation terms. Total energies of the thin film crystal as the function of six components of crystal strain are calculated to find a minimum value. Total energies are calculated discretely and a continuous function approximation is introduced. A sampling area is selected by considering the symmetry between $a$ and $b$ axes in a tetragonal crystal structure. Sampling points are generated by using a latin hypercube sampling (LHS) method (Olsson & Sandberg, 2002), which is the efficient tool to get nonoverlap sapling points. The following global function model is generated by using a kriging polynomial hybrid approximation (KPHA) method (Sakata et al., 2007).
Fig. 3. Crystal structure and orientations of perovskite compounds.

\[ E = A_h \varepsilon_h^2 + B_{ij} \varepsilon_i \varepsilon_j + C_{li} + E_{T0} (h, i, j = a, b, c, ab, bc, ca) \]  (14)

where \( E_{T0} \) is the total energy of the stable crystal, \( \varepsilon_h, \varepsilon_i \) and \( \varepsilon_j \) epitaxial strains and \( A_h, B_{ij} \) and \( C_{li} \) coefficients generated by KPHA method. A gradient of total energy at each sampling point is calculated to generate an approximate quadratic function. The minimum point of a total energy can be found by using this function.

2.2.2 Algorithm of the process crystallographic simulation

In the process crystallographic simulation, it is assumed that several crystal unit cells of crystal clusters, which have certain conformations, can grow on a substrate as shown Fig. 4. The left-hand side diagram in Fig. 4 shows an example of conformation in cases of [001], [100], [110] and [101] orientations, and the right-hand side shows [111] orientation. O, A and B are points of substrate atoms corresponding to thin films ones within the allowable range of distance. \( l_{OA} \) and \( l_{OB} \) indicate distances of A and B from O, respectively. \( \theta_{AOB} \) indicates the angle between lines OA and OB.

Fig. 4. Schematic of crystal conformations on a substrate.
Table 1 summarizes the relationship between the lattice constants of the thin film and $l_{OA}$ and $l_{OB}$ according to crystal orientations. Additionally, Table 1 shows crystal strains, which can be determined in the corresponded crystal orientations. However, particular crystal strains, such as $\varepsilon_i^*$ and $\gamma_{ij}^*$, cannot be determined by employing the lattice constants of the thin film and the geometric constants of the substrate. In this numerical analysis scheme, their unknown components are determined by employing the condition of minimum total energy of the crystal unit cell.

Figure 5 shows the flowchart of the crystal growth prediction algorithm. First, lattice constants of the thin film and the substrate are inputted. The following procedure is demonstrated. Substrate coordinates of A and B points, which are indicated as $(m_A, n_A)$ and $(m_B, n_B)$, are updated according to the numerical result under the condition of fixing O point in order to generate candidate crystal clusters with assumed conformations and orientations. The search range of the crystal cluster is settled as $0 < m_A, m_B < m$ and $0 < n_A, n_B < n$ by considering the grain size of the piezoelectric thin film crystal. $\varepsilon_i$ and $\gamma_{ij}$ as shown in Figure 5 are unit vectors of the substrate coordinate system. Lattice constants of the crystal cluster are compared with geometrical parameters of the substrate, and candidate crystal clusters, which have extreme lattice mismatches, are eliminated. Crystal strains caused by the epitaxial growth are calculated for every candidates of the grown crystal cluster as shown in Table 1. The total energy of grown crystal cluster is estimated by using the total energy as a function of crystal strains. Total energies of candidate crystal clusters are compared with one of the free-strained boundary condition, in order to calculate total energy increments of candidate crystal clusters.

$\varepsilon_i^*$ and $\gamma_{ij}^*$ can be given from first-principles calculation to minimize total energy.

<table>
<thead>
<tr>
<th></th>
<th>[001]</th>
<th>[100]</th>
<th>[110]</th>
<th>[101]</th>
<th>[111]</th>
</tr>
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<tbody>
<tr>
<td>$l_{OA}$</td>
<td>$a$</td>
<td>$c$</td>
<td>$c$</td>
<td>$\sqrt{a^2 + c^2}$</td>
<td>$\sqrt{a^2 + c^2}$</td>
</tr>
<tr>
<td>$l_{OB}$</td>
<td>$b$</td>
<td>$b$</td>
<td>$\sqrt{a^2 + b^2}$</td>
<td>$b$</td>
<td>$\sqrt{b^2 + c^2}$</td>
</tr>
</tbody>
</table>

Epitaxial strain

$\varepsilon_a = \frac{l_{OA}}{ka} - 1$  
$\varepsilon_b = \frac{l_{OB}}{kb} - 1$  
$\varepsilon_c = \frac{l_{OA}}{kc} - 1$  

$\gamma_{ab} = \frac{\theta_{AOB} - \theta_{ab}}{\gamma_{ab}}$  
$\gamma_{bc} = \frac{\theta_{AOB} - \theta_{bc}}{\gamma_{bc}}$  
$\gamma_{ca} = \frac{\theta_{AOB} - \theta_{ca}}{\gamma_{ca}}$  

$\varepsilon_{1}^*$ and $\gamma_{ij}^*$ can be given from first-principles calculation to minimize total energy.
The fraction of crystal cluster grown on the substrate is calculated by a canonical distribution (Nagaoka et al., 1994).

\[
p_i = \frac{\exp\left(-\Delta E_i / k_B T\right)}{\sum_n \exp\left(-\Delta E_n / k_B T\right)}
\]

(15)

Where \(\Delta E\) is the total energy increment of the grown cluster, \(k_B\) the Boltzmann constant and \(T\) the temperature.

### 2.3 Macro continuum structure analysis by using the crystallographic homogenization method

The crystallographic homogenization method scales up micro heterogeneous structure, such as polycrystalline aggregation, to macro homogeneous structure, such as continuum body. The micro heterogeneous structure has the area \(Y\) and microscopic polycrystalline coordinate \(y\), and the macro homogeneous structure has the area \(X\) and macroscopic sample coordinate \(x\). Here, it relates to two scales by using the scale ratio \(\lambda_h\).

---

Fig. 5. Flowchart of the process crystallographic simulation.
where $\lambda_h$ is an extremely small value. Both coordinates of the micro polycrystalline and the macro continuum structures can be selected independently based on the Eq. (16). Coupling variables are affixed to the superscript $\lambda_h$ because the behaviour of the piezo-elastic materials is affected by the polycrystalline structure and $\lambda_h$.

The linear piezo-elastic constitutive equation is described as,

$$\sigma_{ij}^{\lambda_h} = C_{ijkl}^{\lambda_h} e_{kl}^{\lambda_h} - e_{ij}^{\lambda_h} E_{k}^{\lambda_h}$$

(17)

$$D_{ij}^{\lambda_h} = e_{ik}^{\lambda_h} e_{kl}^{\lambda_h} + e_{ii}^{\lambda_h} E_{k}^{\lambda_h}$$

(18)

The equation of the virtual work of piezoelectric material is written as,

$$\int_{\Omega} \left( C_{ijkl}^{\lambda_h} e_{kl}^{\lambda_h} - e_{ij}^{\lambda_h} E_{k}^{\lambda_h} \right) \frac{\partial \delta u_{ij}^{\lambda_h}}{\partial x_j} d\Omega + \int_{\Gamma} \left( e_{ik}^{\lambda_h} e_{kl}^{\lambda_h} + e_{ii}^{\lambda_h} E_{k}^{\lambda_h} \right) \frac{\partial \delta \phi^{\lambda_h}}{\partial x_k} d\Gamma$$

(19)

where the strain tensor and the electric field tensor are

$$\varepsilon_{ij}^{\lambda_h} = \frac{1}{2} \left( \frac{\partial u_i^0(x)}{\partial x_j} + \frac{\partial u_j^0(x)}{\partial x_i} \right)$$

(20)

$$E_{ij}^{\lambda_h} = -\frac{\partial \phi^0(x)}{\partial x_i} - \frac{\partial \phi^0(x,y)}{\partial y_i}$$

(21)

It is assumed that the microscopic displacement and the electrostatic potential can be written as the separation of variables:

$$u_i^1(x,y) = \chi_i^{kl}(x,y) \frac{\partial u_k^0(x)}{\partial x_l} + \Phi_i^{mn}(x,y) \frac{\partial \phi^0(x)}{\partial x_m}$$

(22)

$$\phi^1(x,y) = \Phi_i^{kl}(x,y) \frac{\partial u_k^0(x)}{\partial x_l} + R^k(x,y) \frac{\partial \phi^0(x)}{\partial x_k}$$

(23)

where $\chi_i^{kl}(x,y)$ is the characteristic displacement of a unit cell, $R^k(x,y)$ the characteristic electrical potential of a unit cell and $\Phi_i^{kl}(x,y)$ and $\Phi_i^{mn}(x,y)$ the characteristic coupling functions of a unit cell. The macroscopic dominant equations are described as,

$$\int_{\Omega} \left( C_{ijkl}^{\lambda_h} \frac{\partial \chi_i^{mn}}{\partial x_l} + e_{ij}^{\lambda_h} \frac{\partial \phi_i^{mn}}{\partial y_k} \right) \frac{\partial \delta u_i^1(x,y)}{\partial y_j} dY$$

(24)

$$= -\int_{\Omega} C_{ijkl}^{\lambda_h} \frac{\partial u_i^0(x,y)}{\partial y_j} dY$$

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\[
\int_Y \left( e_{ikl} \frac{\partial \Phi^m_{ij}(x,y)}{\partial y_k} + e_{ik} \frac{\partial \phi^m_{ij}(x,y)}{\partial y_j} \right) \, dY = -\int_Y e_{iimn} \frac{\partial \phi^1_{ij}(x,y)}{\partial y_j} \, dY
\]  
\[\text{Equation (25)}\]

\[
\int_Y \left( e_{ikl} \frac{\partial \Phi^p_{ij}(x,y)}{\partial y_k} + e_{kij} \frac{\partial R^p_{ij}(x,y)}{\partial y_j} \right) \, dY = -\int_Y e_{ipj} \frac{\partial \Phi^1_{ij}(x,y)}{\partial y_j} \, dY
\]  
\[\text{Equation (26)}\]

\[
\int_Y \left( e_{ikl} \frac{\partial \Phi^p_{ij}(x,y)}{\partial y_k} + e_{ik} \frac{\partial R^p_{ij}(x,y)}{\partial y_j} \right) \, dY = \int_Y e_{ip} \frac{\partial \Phi^1_{ij}(x,y)}{\partial y_j} \, dY
\]  
\[\text{Equation (27)}\]

where, $C_{ijkl}$ is the elastic stiffness tensor at constant electric field, $\varepsilon_{ik}$ the dielectric constant tensor at constant strain and $e_{kij}$ the piezoelectric stress constant tensor. They are calculated by experimentally measured crystal properties. Equations (24) - (27) have the solution under the condition of the periodic boundary. The homogenized elastic stiffness tensor, piezoelectric stress constant tensor and dielectric constant tensor are described by the following characteristic function tensor.

\[
C_{ijkl}^{EH} = \frac{1}{|Y|} \int_Y \left( C^{E}_{iimn} + C^{E}_{ikl} \frac{\partial \Phi^m_{ij}(x,y)}{\partial y_k} + e_{ik} \frac{\partial \phi^m_{ij}(x,y)}{\partial y_j} \right) \, dY
\]  
\[\text{Equation (28)}\]

\[
e_{ipj}^{EH} = \frac{1}{|Y|} \int_Y \left( e_{p} + e_{kij} \frac{\partial R^p_{ij}(x,y)}{\partial y_k} + C^{E}_{ikl} \frac{\partial \Phi^p_{ij}(x,y)}{\partial y_j} \right) \, dY
\]  
\[\text{Equation (29)}\]

\[
e_{ip}^{SH} = \frac{1}{|Y|} \int_Y \left( e_{ip} + e_{p} \frac{\partial R^p_{ij}(x,y)}{\partial y_1} - e_{ikl} \frac{\partial \Phi^1_{ij}(x,y)}{\partial y_k} \right) \, dY
\]  
\[\text{Equation (30)}\]

where superscript $H$ means the homogenized value.

The conventional two-scale finite element analysis is based on the crystallographic homogenization method. In this conventional analysis, the virtually determined or experimentally measured orientations are employed for the micro crystalline structure to characterize the macro homogenized piezoelectric properties. However, this conventional analysis can not characterize a new piezoelectric thin film because of unknown crystal structure and material properties.

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A newly proposed three-scale structure analysis can scale up and characterize the crystal structure to the micro polycrystalline and macro continuum structures. First, the stable structure and properties of the new piezoelectric crystal are evaluated by using the first-principles DFT. Second, the crystal growth process of the new piezoelectric thin film is analyzed by using the process crystallographic simulation. The preferred orientation and their fractions of the micro polycrystalline structure are predicted by this simulation. Finally, the homogenized piezoelectric properties of the macro continuum structure are characterized by using the crystallographic homogenization theory. Comparing the provability of crystal growth and the homogenized piezoelectric properties of the new piezoelectric thin film on several substrates, the best substrate is found by using the three-scale structure analysis. It is confirmed that the three-scale structure analysis can design not only existing thin films but also new piezoelectric thin films.

3. Three-scale structure analysis of a new biocompatible piezoelectric thin film

3.1 Crystal structure analysis by using the first-principles calculation

The biocompatible elements (Ca, Cr, Cu, Fe, Ge, Mg, Mn, Mo, Na, Ni, Sn, V, Zn, Si, Ta, Ti, Zr, Li, Ba, K, Au, Rb, In) were assigned to A cation in the perovskite-type compound ABO₃. Silicon, which was one of well-known biocompatible elements, was employed on B cation. Values of tolerance factor were calculated by using Pauling’s ionic radius. Five silicon oxides satisfied the geometrical compatibility condition, where MgSiO₃ = 0.88, MnSiO₃ = 0.93, FeSiO₃ = 0.91, ZnSiO₃ = 0.91 and CaSiO₃ = 1.01. The stable cubic structure with minimum total energy was calculated for the five silicon oxides. As the cubic structure has a feature of high symmetry, the stable crystal structure was easy to estimate because of a little dependency on the initial atomic coordinates. Table 2 shows the lattice constants of the silicon oxide obtained by the first-principles DFT. The phonon properties of cubic structure at paraelectric non-polar phase were calculated to consider phase transition to other crystal structures. Table 3 summarizes the eigenfrequency, the phonon vibration mode and the eigenvector components normalized to unity. MgSiO₃, MnSiO₃, FeSiO₃, ZnSiO₃ showed negative values of eigenfrequency. Cubic structures of these four silicon oxides became unstable owing to softening atomic vibration, and they had possibility of the phase transition to other crystal structure. On the other hand, the stable structure of CaSiO₃ was the cubic structure due to positive value of eigenfrequency. The phonon vibration modes are also summarized in Table 3. All eigenvectors of MgSiO₃, MnSiO₃ and FeSiO₃ were almost parallel to c axis in crystallographic coordinate system. These three silicon oxides had a high possibility to change from the cubic structure to the tetragonal structure, which showed superior piezoelectricity. The eigenvector of O₁ and O₁₁ in ZnSiO₃, however, included a component perpendicular to c axis. It was expected that ZnSiO₃ changed from cubic structure to other structures consisting of a rotated SiO₆-octahedron, such as the orthorhombic structure with inferior piezoelectricity. The stable tetragonal structure to minimize the total energy was calculated for the above three silicon oxides, MgSiO₃, MnSiO₃ and FeSiO₃. Total energies of these tetragonal structures were lower than those of the stable cubic structure. Table 4 shows lattice constants and internal coordinates of constituent atoms. In comparison of the aspect ratio among the three silicon oxides, the value of MgSiO₃ was larger than 1.0. On the other hand,
the aspect ratio of MnSiO$_3$ and FeSiO$_3$ were smaller than 1.0. Generally, the tetragonal structure of typical perovskite-type oxides such as BaTiO$_3$ and PbTiO$_3$ had larger aspect ratio than 1.0. Consequently, the tetragonal structure of MnSiO$_3$ and FeSiO$_3$ could not be existed. The above results have indicated that MgSiO$_3$ was a remarkable candidate for the new biocompatible piezoelectric material.

<table>
<thead>
<tr>
<th>Material</th>
<th>Lattice constant (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgSiO$_3$</td>
<td>0.3459</td>
</tr>
<tr>
<td>MnSiO$_3$</td>
<td>0.3431</td>
</tr>
<tr>
<td>FeSiO$_3$</td>
<td>0.3421</td>
</tr>
<tr>
<td>ZnSiO$_3$</td>
<td>0.3454</td>
</tr>
<tr>
<td>CaSiO$_3$</td>
<td>0.3520</td>
</tr>
</tbody>
</table>

Table 2. The lattice constants of cubic structure for candidates of the piezoelectric material.

<table>
<thead>
<tr>
<th>Material</th>
<th>Eigenfrequency (cm$^{-1}$)</th>
<th>Phonon eigenvector components</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgSiO$_3$</td>
<td>-112</td>
<td>O$_I$ 0.00 0.00 -0.37</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O$_{II}$ 0.00 0.00 -0.37</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O$_{III}$ 0.00 0.00 -0.22</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Si 0.00 0.00 -0.13</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mg 0.00 0.00 0.88</td>
</tr>
<tr>
<td>MnSiO$_3$</td>
<td>-41</td>
<td>O$_I$ -0.09 0.00 -0.53</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O$_{II}$ -0.07 0.00 -0.53</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O$_{III}$ -0.09 0.00 -0.41</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Si -0.07 0.00 -0.45</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mn 0.04 0.00 0.23</td>
</tr>
<tr>
<td>FeSiO$_3$</td>
<td>-83</td>
<td>O$_I$ 0.08 0.01 -0.32</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O$_{II}$ 0.04 0.00 -0.32</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O$_{III}$ 0.08 0.00 -0.17</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Si 0.03 0.00 -0.13</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fe -0.22 -0.02 0.83</td>
</tr>
<tr>
<td>ZnSiO$_3$</td>
<td>-267</td>
<td>O$_I$ 0.24 0.00 -0.66</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O$_{II}$ 0.00 -0.05 0.66</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O$_{III}$ -0.24 0.05 0.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Si 0.00 0.00 0.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zn 0.00 0.00 0.00</td>
</tr>
<tr>
<td>CaSiO$_3$</td>
<td>238</td>
<td>O$_I$ 0.00 0.00 -0.35</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O$_{II}$ 0.01 0.00 -0.35</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O$_{III}$ 0.01 0.00 0.29</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Si -0.01 0.00 0.79</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ca 0.00 0.00 -0.23</td>
</tr>
</tbody>
</table>

Table 3. Comparison of phonon properties of cubic structure among MgSiO$_3$, MnSiO$_3$, FeSiO$_3$, ZnSiO$_3$ and CaSiO$_3$. 

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<table>
<thead>
<tr>
<th></th>
<th>MgSiO$_3$</th>
<th>MnSiO$_3$</th>
<th>FeSiO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice constant</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(nm)</td>
<td>$a = b = 0.3449$</td>
<td>$a = b = 0.3547$</td>
<td>$a = b = 0.3602$</td>
</tr>
<tr>
<td></td>
<td>$c = 0.3538$</td>
<td>$c = 0.3440$</td>
<td>$c = 0.3349$</td>
</tr>
<tr>
<td>Aspect ratio</td>
<td>1.026</td>
<td>0.970</td>
<td>0.930</td>
</tr>
</tbody>
</table>

Table 4. Lattice constants and internal coordinates of constituent atoms for tetragonal structure of MgSiO$_3$, MnSiO$_3$ and FeSiO$_3$.

<table>
<thead>
<tr>
<th></th>
<th>Mg</th>
<th>Si</th>
<th>O$_I$</th>
<th>O$_{II}$</th>
<th>O$_{III}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Z'_{11}$</td>
<td>2.331</td>
<td>3.995</td>
<td>-3.024</td>
<td>-1.620</td>
<td>-1.682</td>
</tr>
<tr>
<td>$Z'_{22}$</td>
<td>2.331</td>
<td>3.995</td>
<td>-1.620</td>
<td>-3.024</td>
<td>-1.682</td>
</tr>
<tr>
<td>$Z'_{33}$</td>
<td>2.254</td>
<td>4.054</td>
<td>-1.637</td>
<td>-1.637</td>
<td>-3.035</td>
</tr>
</tbody>
</table>

Table 5. Born effective charge in tetragonal structure of MgSiO$_3$ perovskite.

<table>
<thead>
<tr>
<th></th>
<th>MgSiO$_3$</th>
<th>BaTiO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spontaneous polarization (C/m$^2$)</td>
<td>$p^S_3$</td>
<td>0.471</td>
</tr>
<tr>
<td>Piezoelectric stress constant (C/m$^2$)</td>
<td>$e_{33}$</td>
<td>4.57</td>
</tr>
<tr>
<td></td>
<td>$e_{31}$</td>
<td>-2.20</td>
</tr>
<tr>
<td></td>
<td>$e_{13}$</td>
<td>12.77</td>
</tr>
</tbody>
</table>

Table 6. Comparison of the spontaneous polarization and piezoelectric stress constant between MgSiO$_3$ and BaTiO$_3$.

Table 5 shows Born effective charges of each atoms of MgSiO$_3$. Piezoelectric properties, including the spontaneous polarization and piezoelectric stress constants $e_{31}$, $e_{33}$ and $e_{13}$, were calculated by these Born effective charges. Table 6 summarizes piezoelectric properties of MgSiO$_3$, those of BaTiO$_3$ calculated by the DFT and observed by the experiment. It could be concluded that MgSiO$_3$ had larger spontaneous polarization than one of BaTiO$_3$. MgSiO$_3$ showed good piezoelectric properties, which were $e_{33} = 4.57$ C/m$^2$, $e_{31} = -2.20$ C/m$^2$ and $e_{13} = 12.77$ C/m$^2$. 

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3.2 Investigation of the best substrate of the biocompatible piezoelectric material MgSiO₃

Three biocompatible atoms, which include Au, Mo and Fe, were selected for the substrate candidate. This is because;
1. these atoms can be used for the under electrode.
2. chemical elements of these atoms have the cubic crystal structure.
Lattice constants of Au with FCC cubic structure are \( a = b = c = 0.4080 \) nm, and ones of Mo with BCC cubic structure are \( a = b = c = 0.3147 \) nm. Ones of Fe with BCC cubic structure are \( a = b = c = 0.2690 \) nm.

Crystal growth process of MgSiO₃ thin film on (100) and (111) facets of candidate substrates were demonstrated by using the process crystallographic simulation. Tables 7 - 9 show numerical results of MgSiO₃ thin film grown on (100) facets of these four substrates, and Tables 10 - 12 show results of one on (111) facets of the substrates.

Table 13 shows summary of the orientation fractions of MgSiO₃ thin film on substrates calculated by canonical distribution. In the case of Mo(100) substrate as shown in Table 8, MgSiO₃[001] and [001] were grown, and their orientation fraction were 61.5 % and 38.5 %, respectively. MgSiO₃[001] was grown on Au(100) and Fe(100) at 100 % probability. Comparing total energy increments of crystal clusters of MgSiO₃ grown on these substrates, MgSiO₃[001] on Fe(100) substrate was more stable due to the lowest total energy increment as shown in Table 9. MgSiO₃[111] was grown on Au(111) and Mo(111) substrates at 100 % probability.

<table>
<thead>
<tr>
<th>Orientation</th>
<th>[001]</th>
<th>[001]</th>
<th>[001]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \varepsilon_a ) (%)</td>
<td>0.21</td>
<td>0.48</td>
<td>0.64</td>
</tr>
<tr>
<td>( \varepsilon_b ) (%)</td>
<td>0.21</td>
<td>0.48</td>
<td>0.64</td>
</tr>
<tr>
<td>( \varepsilon_c ) (%)</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>( \gamma_{ab} ) (%)</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>( \gamma_{bc} ) (%)</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>( \gamma_{ca} ) (%)</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Total energy of the unit cell (eV)</td>
<td>-2398.4025</td>
<td>-2398.3984</td>
<td>-2398.3946</td>
</tr>
<tr>
<td>Total energy increment (eV)</td>
<td>0.0749</td>
<td>0.1257</td>
<td>0.3158</td>
</tr>
</tbody>
</table>

Table 7. Analytical results for stable conformations and preferred orientations of MgSiO₃ thin film grown on Au(100) substrate.

<table>
<thead>
<tr>
<th>Orientation</th>
<th>[100]</th>
<th>[001]</th>
<th>[001]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \varepsilon_a ) (%)</td>
<td>0.00</td>
<td>1.13</td>
<td>-0.50</td>
</tr>
<tr>
<td>( \varepsilon_b ) (%)</td>
<td>1.13</td>
<td>1.13</td>
<td>-0.50</td>
</tr>
<tr>
<td>( \varepsilon_c ) (%)</td>
<td>-1.41</td>
<td>-0.50</td>
<td>0.00</td>
</tr>
<tr>
<td>( \gamma_{ab} ) (%)</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>( \gamma_{bc} ) (%)</td>
<td>0.00</td>
<td>-0.50</td>
<td>0.00</td>
</tr>
<tr>
<td>( \gamma_{ca} ) (%)</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Total energy of the unit cell (eV)</td>
<td>-2398.3803</td>
<td>-2398.3772</td>
<td>-2398.3979</td>
</tr>
<tr>
<td>Total energy increment (eV)</td>
<td>0.0925</td>
<td>0.1046</td>
<td>0.4447</td>
</tr>
</tbody>
</table>

Table 8. Analytical results for stable conformations and preferred orientations of MgSiO₃ thin film grown on Mo(100) substrate.
Comparing total energy increments of crystal clusters of MgSiO$_3$ grown on these two substrates, Au(111) was better substrate than Mo(111) due to low total energy increment. MgSiO$_3$(111) and [001] on Fe(111) were grown at 97.8% and 2.2% probability, respectively. Consequently, it could be concluded that four substrates, which included Mo(100), Fe(100) and (111), Au(111), were candidates of the best substrate for MgSiO$_3$ thin film.

<table>
<thead>
<tr>
<th>Orientation</th>
<th>[001]</th>
<th>[001]</th>
<th>[001]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_a$ (%)</td>
<td>-0.11</td>
<td>0.29</td>
<td>-0.56</td>
</tr>
<tr>
<td>$\varepsilon_b$ (%)</td>
<td>-0.11</td>
<td>0.29</td>
<td>-0.56</td>
</tr>
<tr>
<td>$\varepsilon_c$ (%)</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>$\gamma_{ab}$ (%)</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>$\gamma_{bc}$ (%)</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>$\gamma_{ca}$ (%)</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Total energy of the unit cell (eV)</td>
<td>-2398.4032</td>
<td>-2398.4016</td>
<td>-2398.3966</td>
</tr>
<tr>
<td>Total energy increment (eV)</td>
<td>0.0060</td>
<td>0.0906</td>
<td>0.1092</td>
</tr>
</tbody>
</table>

Table 9. Analytical results for stable conformations and preferred orientations of MgSiO$_3$ thin film grown on Fe(100) substrate.

<table>
<thead>
<tr>
<th>Orientation</th>
<th>[111]</th>
<th>[001]</th>
<th>[111]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_a$ (%)</td>
<td>2.55</td>
<td>0.06</td>
<td>1.50</td>
</tr>
<tr>
<td>$\varepsilon_b$ (%)</td>
<td>2.55</td>
<td>0.06</td>
<td>1.50</td>
</tr>
<tr>
<td>$\varepsilon_c$ (%)</td>
<td>-0.03</td>
<td>0.00</td>
<td>-1.05</td>
</tr>
<tr>
<td>$\gamma_{ab}$ (%)</td>
<td>-0.50</td>
<td>2.20</td>
<td>0.00</td>
</tr>
<tr>
<td>$\gamma_{bc}$ (%)</td>
<td>-0.50</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>$\gamma_{ca}$ (%)</td>
<td>-0.50</td>
<td>0.00</td>
<td>2.20</td>
</tr>
<tr>
<td>Total energy of the unit cell (eV)</td>
<td>-2398.2686</td>
<td>-2398.3450</td>
<td>-2398.3546</td>
</tr>
<tr>
<td>Total energy increment (eV)</td>
<td>0.5393</td>
<td>2.1038</td>
<td>2.3891</td>
</tr>
</tbody>
</table>

Table 10. Analytical results for stable conformations and preferred orientations of MgSiO$_3$ thin film grown on Au(111) substrate.

<table>
<thead>
<tr>
<th>Orientation</th>
<th>[111]</th>
<th>[111]</th>
<th>[001]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_a$ (%)</td>
<td>0.73</td>
<td>0.93</td>
<td>-0.50</td>
</tr>
<tr>
<td>$\varepsilon_b$ (%)</td>
<td>0.73</td>
<td>0.93</td>
<td>-1.53</td>
</tr>
<tr>
<td>$\varepsilon_c$ (%)</td>
<td>-1.81</td>
<td>-1.61</td>
<td>0.50</td>
</tr>
<tr>
<td>$\gamma_{ab}$ (%)</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>$\gamma_{bc}$ (%)</td>
<td>0.00</td>
<td>0.00</td>
<td>0.50</td>
</tr>
<tr>
<td>$\gamma_{ca}$ (%)</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Total energy of the unit cell (eV)</td>
<td>-2398.3724</td>
<td>-2398.3717</td>
<td>-2398.3796</td>
</tr>
<tr>
<td>Total energy increment (eV)</td>
<td>0.7738</td>
<td>1.5518</td>
<td>1.9276</td>
</tr>
</tbody>
</table>

Table 11. Analytical results for stable conformations and preferred orientations of MgSiO$_3$ thin film grown on Mo(111) substrate.
Table 12. Analytical results for stable conformations and preferred orientations of MgSiO$_3$ thin film grown on Fe(111) substrate.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Atom</th>
<th>Facet</th>
<th>MgSiO$_3$ Orientation</th>
<th>Fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>(100)</td>
<td>[001]</td>
<td>100.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(111)</td>
<td>[111]</td>
<td>100.0</td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>(100)</td>
<td>[100]</td>
<td>61.5</td>
<td>38.5</td>
</tr>
<tr>
<td></td>
<td>(100)</td>
<td>[001]</td>
<td>38.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(111)</td>
<td>[111]</td>
<td>100.0</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>(100)</td>
<td>[001]</td>
<td>100.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(111)</td>
<td>[111]</td>
<td>97.8</td>
<td>2.2</td>
</tr>
</tbody>
</table>

Table 13. Analytical results of preferred orientations and their fractions for MgSiO$_3$ thin films grown on various substrates.

Analytically determined piezoelectric stress constants and orientation fractions of MgSiO$_3$ were introduced into the macro continuum structure analysis. Homogenized piezoelectric strain constants of the MgSiO$_3$ thin film on four substrate candidates were calculated.

Fig. 6. Homogenized piezoelectric stress constant of MgSiO$_3$ thin film on various substrates.
Figure 6(a) shows homogenized $e_{31}$ constants and Fig. 6(b) $e_{33}$. Substrates, facets of substrates and orientation fractions of MgSiO$_3$ thin film were also shown in figures. MgSiO$_3$[111] on Au(111) substrate indicated the highest piezoelectric stress constants, $e_{31} = -3.65$ C/m$^2$ and $e_{33} = 5.10$ C/m$^2$. MgSiO$_3$[001] on Fe(100) showed $e_{31} = -2.20$ C/m$^2$ and $e_{33} = 4.57$ C/m$^2$. $e_{31}$ of MgSiO$_3$[001] on Fe(100) was 39.7 % lower than one on Au(111) and $e_{33}$ of MgSiO$_3$[001] on Fe(100) was 10.4 % lower than one on Au(111). In the case of Fe(111) substrate, $e_{31}$ was equal to one on Au(111) substrate, however $e_{33}$ was smaller than one on Au(111). Furthermore, MgSiO$_3$ on Au(111) was more stable than one on Fe(111) substrate. These results have concluded that Au(111) was the best substrate for MgSiO$_3$ thin film.

4. A new biocompatible piezoelectric MgSiO$_3$ thin film generation

4.1 Experimental method

MgSiO$_3$ thin film is generated by radio-frequency magnetron sputtering. Three factors are selected for generating perovskite tetragonal structure and high piezoelectric property. These conditions are i) the substrate temperature $T_s$, ii) the post-annealing temperature $T_a$ and iii) flow rate of oxygen $f_{O2}$. This is because that i) the substrate temperature contributes configuration and bonding of thin film crystals, and ii) the post-annealing temperature affects crystallization of amorphous crystal. iii) The flow rate of oxygen affects crystal morphology and composition of the MgSiO$_3$ crystal. These generation conditions are set as $T_s = 300$ ºC, 350 ºC, 400 ºC, $T_a = 600$ ºC, 650 ºC, 700 ºC, and $f_{O2} = 1.0$ sccm, 3.0 sccm, 5.0 sccm, respectively. The target material is used the mixed sinter of MgO and SiO$_2$, the substrate is Au(111)/SrTiO$_3$(110), which is determined by the three-scale structure analysis. The electric power is 100 W, flow rate of Ar gas is 10 sccm and the pressure in chamber during the sputtering is 0.5 Pa. Thin film is sputtered 4 hours and post-annealed an hour after sputtering.

The displacement–voltage curve of MgSiO$_3$ thin film is measured by ferroelectric characterization (FCE) system. Generally, displacement-voltage curve of the piezoelectric material shows butterfly-type hysteresis curve. The piezoelectric strain constant $d_{33}$ can be calculated by gradient of the butterfly-type hysteresis curve. The response surface methodology (RSM) (Berger & Maurer, 2002) is employed to find the optimum combination of generation factor levels of the MgSiO$_3$ thin film.

4.2 Generation of the new biocompatible piezoelectric MgSiO$_3$ thin film

Displacement-voltage curves under the conditions of $f_{O2} = 1.0, 3.0$ and 5.0 sccm are shown in Fig. 7 - 9. All thin films showed the piezoelectric property due to butterfly-type hysteresis curves. The piezoelectric strain constant $d_{33}$ can be calculated by the gradient at cross point of the butterfly-type hysteresis curve, and $d_{33}$ was indicated in all graphs. $d_{33}$ constants of all thin films were larger than the $d_{33}$ constant ($= 129.4$ pm/V) of BaTiO$_3$, which was commonly used lead-free piezoelectric material generated in our previous study.

The optimum conditions for generating the MgSiO$_3$ thin film were found by using RSM. Figure 10 shows the response surface of $d_{33}$ constant as a function of $T_s$ and $T_a$ under the condition of $f_{O2}$= 4.0 sccm. Figure 10(a) shows the aerial view and Fig. 10(b) top view. The black point indicates the highest point of $d_{33}$ constant. The optimum condition, for $T_s$ = 300 ºC, $T_a$ = 631 ºC and $f_{O2}$= 4.0 sccm, was found.
MgSiO₃ thin film was generated at \( T_s = 250 \, ^\circ\mathrm{C} \), because the obtained best \( T_s \) was lowest temperature in the range of the substrate temperature which was set in this study. However, the displacement-voltage curves were not indicated the butterfly-type hysteresis curve. This is because the thin film was not crystallized to MgSiO₃ due to inactive adatoms and low collision rate of adatoms.

Fig. 7. Displacement-voltage curves of MgSiO₃ thin films in the case of \( f_{O_2} = 1.0 \, \text{sccm} \).

Fig. 8. Displacement-voltage curves of MgSiO₃ thin films in the case of \( f_{O_2} = 3.0 \, \text{sccm} \).
Fig. 9. Displacement-voltage curves of MgSiO₃ thin films in the case of $f_{O_2} = 5.0$ sccm.

Fig. 10. Piezoelectric strain constant $d_{33}$ as functions of $T_s$ and $T_a$ in the case of $f_{O_2} = 4.0$ sccm.
Three-Scale Structure Analysis Code and Thin Film Generation of a New Biocompatible Piezoelectric Material MgSiO₃

Finally, MgSiO₃ thin film was generated at the optimum condition. Figure 11 shows its displacement-voltage curve. $d_{33}$ constant was obtained as 359.2 pm/V and this value was higher than one of the pure PZT thin films, $d_{33} = 307.0$ pm/V, generated by Z. Zhu et al (Zhu et al, 2010).

Consequently, the piezoelectric MgSiO₃ thin film was generated successfully and it can be used for sensors and actuators for MEMS or NENS.

5. Conclusion

In this study, the three-scale structure analysis code, which is based on the first-principles density functional theory (DFT), the process crystallographic simulation and the crystallographic homogenization theory, was newly developed. Consequently, a new biocompatible MgSiO₃ piezoelectric material was generated by using the radio-frequency (RF) magnetron sputtering system, where its optimum generating condition has been found analytically and experimentally.

Section 2 discussed the algorithm of the three-scale structure analysis, which can design epitaxially grown piezoelectric thin films. This analysis was constructed in three-scale structures, such as a crystal structure, a micro polycrystalline structure and a macro continuum structure. The existing two-scale analysis could evaluate the property of the macro continuum structure by using experimentally observed information of crystal structure, such as crystallographic orientation and properties of the crystal. The three-scale structure analysis can design new biocompatible piezoelectric thin films through three steps, which were to calculate the crystal structure by using the first-principles DFT, to evaluate the epitaxial growth process by using crystallographic simulation, and to calculate the homogenized properties of thin film by using the crystallographic homogenization theory.

In section 3, in order to find a new biocompatible piezoelectric crystal and its best substrate, the three-scale structure analysis was applied to the silicon oxides. Consequently, MgSiO₃ had a large spontaneous polarization $P_{s}^{0} = 0.471$ C/m² and it could present good piezoelectric stress constants $e_{33} = 4.57$ C/m², $e_{31} = -2.20$ C/m² and $e_{15} = 12.77$ C/m². These results indicated that MgSiO₃ was one of the candidates of the new biocompatible piezoelectric thin film. Au(111) was the best substrate of MgSiO₃ thin film, because MgSiO₃[111] on Au(111) was most stable and showed highest piezoelectric stress constant $e_{31} = -3.65$ C/m² and $e_{33} = 5.10$ C/m².
In section 4, MgSiO$_3$ piezoelectric thin film was generated by using the RF magnetron sputtering system. The optimum condition was found by using the response surface methodology (RSM). Measuring the piezoelectric properties of the thin films by using the ferroelectric character evaluation (FCE) system, all MgSiO$_3$ thin films showed the piezoelectric property due to butterfly-type hysteresis curves. Finally, the optimum condition for $T_s = 300 \degree C$, $T_a = 631 \degree C$ and $f_{O_2} = 4.0$ sccm, was found and the best piezoelectric strain constant $d_{33} = 359.2$ pm/V was obtained. This value was higher than the one of the pure PZT thin films, $d_{33} = 307.0$ pm/V, generated by Z. Zhu et al.. Consequently, the piezoelectric MgSiO$_3$ thin film was generated successfully and it can be used for sensors and actuators for MEMS or NENS.

6. References


Fu, P., Xu, Z., Chu, R., Li, W., Zhang, G. & Hao, J. (2010). Piezoelectric, Ferroelectric and Dielectric Properties of La$_2$O$_3$-doped (Bi$_{0.5}$Na$_{0.5}$)$_{0.94}$Ba$_{0.06}$TiO$_3$ Lead-Free Ceramics, *Materials and Design*, Vol.31, (May 2009), pp.796-801, 0261-3069.


In modern research and development, materials manufacturing crystal growth is known as a way to solve a wide range of technological tasks in the fabrication of materials with preset properties. This book allows a reader to gain insight into selected aspects of the field, including growth of bulk inorganic crystals, preparation of thin films, low-dimensional structures, crystallization of proteins, and other organic compounds.

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