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SPACE CHARGE INDUCED FLEXOELECTRIC TRANSDUCERS FOR ENERGY HARVESTING

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ABSTRACT

Lead zirconate titanate (PZT) is widely used in energy harvesting because of its excellent material properties. However, as the material contains lead, there are significant environmental concerns with its production and use. Flexoelectricity refers to the coupling between strain gradient and electric polarization that exists, in principle, in all dielectric materials and would allow for energy harvesting without using piezoelectric materials. However, the effect is very weak in most materials. Promisingly, it has recently been shown that space charge polarized materials (i.e., semiconducting materials with insulating barrier layers) can exhibit enhanced flexoelectricity. This space charge induced flexoelectric effect opens up the possibility of a non-toxic replacement for PZT in energy harvesting applications. In this paper we investigate the use of doped silicon with hafnium oxide insulating layers as flexoelectric transducers that could replace PZT in many applications including energy harvesting. Specifically, we experimentally demonstrate flexoelectricity in a bending beam and show an effective flexoelectric coefficient of 4.9 $\mu C/m$. Finally, we develop and demonstrate a finite element model for flexoelectricity.

KEYWORDS

Energy harvesting, Flexoelectricity, Piezoelectricity, Space charge polarization.

INTRODUCTION

Lead zirconate Titanate (PZT) is a widely used material in a variety of applications requiring electromechanical transduction, including energy harvesting. The lead contained in the PZT represents an environmental risk all along the value chain (i.e. mining to end device disposal) and is increasingly subject to health, safety, and environmental legislation [1] . Despite decades of research effort, no good, environmentally friendly drop-in replacement for PZT has been found.

Flexoelectricity is a size-dependent electromechanical effect that generally refers to the coupling between the strain gradient and electric polarization in which the strain gradient breaks the inversion symmetry and induces an electric response. Based on linear continuum theory of flexoelectricity, the electric polarization P in a linear dielectric is

$$P_i = \chi_{ij} E_j + \mu_{klij} \nabla_j \varepsilon_{kl} \qquad (1)$$

where E_j is the electric field component, ε is the mechanical strain tensor, χ is the second-order dielectric susceptibility tensor, and μ is the fourth-order tensor of flexoelectric coefficients. Although the effect was discovered several decades ago, it did not gain much attention since the effect was found to be insignificant at the macroscopic level. The induced polarization scales with strain gradient. Furthermore, the flexoelectric coefficient scales with dielectric permittivity [2]. Therefore, it is possible to improve the flexoelectric induced polarization by enhancing both the dielectric permittivity and the strain gradient.

A bending beam produces a strain gradient through its thickness as a result of an externally applied force. However, except for beams with sub-micron thickness, the achievable strain gradients are too small to achieve a significant electrical polarization [3]. However, larger strain gradients can be achieved by compressing a truncated pyramid as shown by Cross [4]. The flexoelectric effect also scales with the dielectric permittivity. Space charge polarization refers to the electrical polarization of a material that occurs when charge carriers can migrate an appreciable distance before being blocked by an insulating interface. Space charge structures can have an effective dielectric permittivity as high as ~100,000 and can exhibit flexoelectric-like behavior. Figure 1 illustrates the space charge induced flexoelectric (SCIF) effect in a semiconducting medium with dielectric interface layers. Recently, Narvaez et al. [5] demonstrated that bending semiconducting barium strontium titanate (BST) with mobile charges can induce flexoelectric coefficients as high as two orders of magnitude beyond the already-large coefficients of BST. Their demonstrated flexoelectric coefficient (nearly $1000\,\mu C m^{-1}$) is the largest so far reported. Based on the fact that space charge polarization in semiconductors can generate a flexoelectric-like response with effective flexoelectric coefficients larger than insulators, it is possible that transducers made of semiconducting materials with insulating interfaces fabricated into truncated pyramid structures could exhibit a large flexoelectric response.

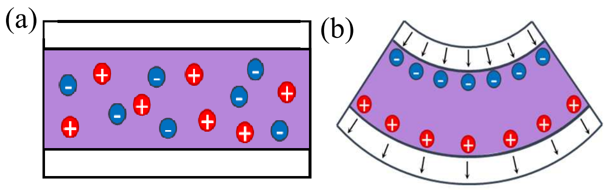

Figure 1: Illustration of space charge induced flexoelectric (SCIF) effect. (a) SCIF structure: semiconducting bulk with dielectric interface layers on each side. Note, although both positive and negative mobile charge carriers are shown, the bulk can be either p- or n-type. (b) Illustration of space charge polarization resulting from strain gradient.

In this paper we present experimental verification of the SCIF effect using a doped silicon cantilever beam with hafnium oxide (HfO_2) insulating layers. We report on the development and initial demonstration of a computational system to model and further investigate the physics of flexoelectric transducers, primarily those based on arrays of truncated pyramids.

EXPERIMENTAL DEMONSTRATION

To examine the effectiveness of space charge induced flexoelectricity, we experimentally measured the flexoelectric coefficient of a beam (1cm long, 5cm wide, and 500 μm thick), with an insulating HfO_2 layer of 30 nm on both silicon surfaces (see Figure 2).

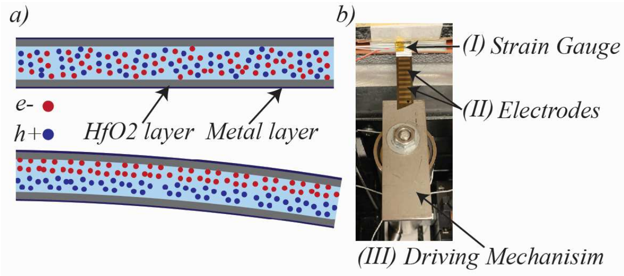

Figure 2: a) Schematic showing space charge polarization resulting from strain gradient (bending in this case) in a cantilever beam. b) Photograph of the arrangement used to measure the flexoelectric coefficient (μ_{3333}) of a silicon-based barrier layer capacitor flexoelectric beam. Strain gauges are visible at the root of the cantilever. A piezoelectric stack actuator in the foreground is used to provide a controlled strain gradient to the sample.

Oscillatory bending stress was delivered to the beam and the strain gradient-induced displacement currents were measured by a lock-in amplifier. Figure 3 shows the flexoelectric polarization driven by the strain gradient in the beam. The effective permittivity of the beam is 35,000 due to space charge polarizability, and the average effective flexoelectric coefficient was 4.9 +/- 0.4 μCm^{-1}. We anticipate that by optimizing the geometry and composition of the barrier layer as well as the conductivity of the Si, it may be possible to increase the effective permittivity and the flexoelectric coefficient by another order of magnitude.

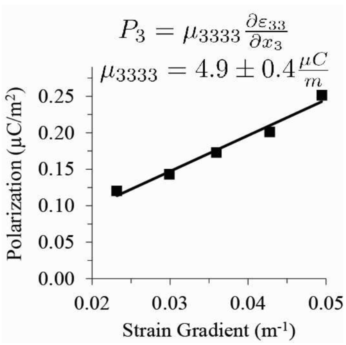

Figure 3: Direct flexoelectric effect. Flexoelectric coefficient (μ_{3333}) is measured experimentally for HfO_2/Si cantilevers.

PYRAMIDAL TRANSDUCER

As mentioned, the flexoelectric effect would be significant only in beams with very low thicknesses [3], which might be difficult to achieve in practice. As an alternative, truncated pyramidal structures as illustrated in Figure 4 can achieve a high strain gradient [4].

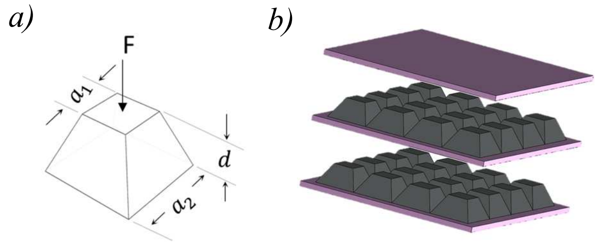

Figure 4: Illustration of 3D pyramidal array transducer. a) Pyramid loaded in compression resulting in a strain gradient and flexoelectric charge separation. b) 3-dimesional SCIF pyramid arrays in silicon.

In order to compare the flexoelectric material and structure performance to piezoelectric materials, Cross [4] proposed calculating an effective piezoelectric charge coefficient, d, of truncated pyramids based on the flexoelectric coefficient, material stiffness, and pyramid geometry [4]. Assuming that the material has a single a nonzero longitudinal flexoelectric coefficient μ_{11}. Based on equation (1), the resulting polarization is

$$P_3 = \mu_{11} \frac{\partial \varepsilon_{33}}{\partial x_3} \tag{2}$$

Linearly interpolating the strain in a truncated pyramid in which the top square face has length a_1 and the bottom square face has length a_2, it is possible to rewrite the above equations as

$$P_3 = \mu_{11} \frac{{a_2}^2 - {a_1}^2}{d c_{11} {a_1}^2} T_3 \tag{3}$$

where c_{11} and d are elastic constant and the pyramid height respectively and T_3 is the stress at the bottom surface as a result of the mechanical load (F) that is $T_3 = \frac{F}{{a_2}^2}$. The resulting electrical polarization in a piezoelectric solid with the same geometry is $P_3 = d_{33} T_3$ in which d_{33} is the piezoelectric charge coefficient. Equating the polarization in the flexoelectric pyramid with the polarization in the piezoelectric solid, one can obtain the effective piezoelectric charge coefficient as

$$d_{33} = \mu_{11} \frac{{a_2}^2 - {a_1}^2}{h c_{11} {a_1}^2} \tag{4}$$

Figure 5 shows calculations for the effective d coefficient compared to PZT-5A as a function of pyramid height (h) for different pyramid base lengths (a_2) assuming $\mu = 100\ \mu Cm^{-1}$ and that the angle of the pyramid is 54.7 degrees following the silicon crystal planes. With reasonable geometries (i.e. pyramid thickness of 20 μm and pyramid base length of 50 – 100 μm), effective d values an order of magnitude larger than PZT-5A are possible. Even with flexoelectric coefficients well below 100 μCm^{-1} significant improvements over PZT-5A are possible.

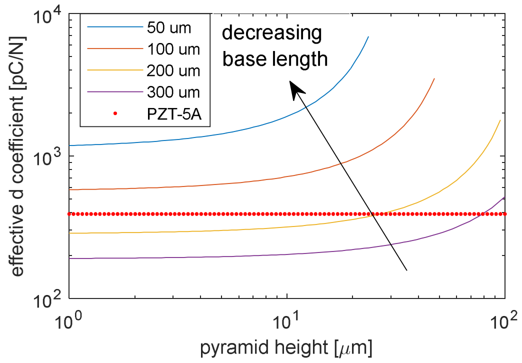

Figure 5: Effective d coefficient for flexoelectric pyramids vs pyramid height for 4 pyramid base lengths. Only bottom to top area ratios less than 10 allowed.

The pyramidal structures analyzed and tested by Cross [4] were made of non-semiconducting BST which is very challenging to micromachine. Implementing SCIF transducers with doped silicon, on the other hand, affords the promise of transducers such as those illustrated in Figure 4 with very high effective piezoelectric coefficients made from non-toxic materials that are easily amenable to micromachining.

MODELING RESULTS

Admittedly, the analogy implied by Cross when calculating an effective piezoelectric charge coefficient may not fully reflect the behavior of a large array of pyramids when implemented in a transducer. Therefore, in this section, we calculate the effective piezoelectric charge coefficient using a 3D finite element simulation.

Numerical study of flexoelectricity is relatively rare since the equations involve high-order spatial derivatives. Some numerical results on flexoelectricity in 2D [6], [7] and 3D [8], [9] have been reported recently. However, there is currently no publicly available finite element (FE) code that models bulk flexoelectricity. Furthermore, in order to fully study the SCIF effect, mobile charge carrier diffusion equations would need to be added to the models. As a first step, in this study, we developed a three-dimensional finite element model in FEniCs [10]–[12] (an open source computing platform) that can simulate bulk flexoelectricity. We developed a tetrahedron element in which the three components of displacement are interpolated using quadratic Lagrangian shape functions and the electric potential is interpolated using linear Lagrangian shape functions. We applied this FE model to a truncated pyramid made of BST (see material properties in table 1) similar to the structure proposed in [13] and calculated an effective piezoelectric charge coefficient.

Table 1: BST material properties.

c_{11}	μ_{11}	χ
$22.67 Gpa$	$121\ \mu C m^{-1}$	$141.6\ nCV m^{-1}$

Figure 6 shows the results of the 3D simulation of the truncated pyramid under compression. The simulation predicts an induced voltage of -0.88V on the top electrode. With this voltage, the resulting effective piezoelectric charge coefficient is $6.0\ pC/N$. The predicted value matches the value reported by other studies [13] lending confidence to the accuracy of the FE model.

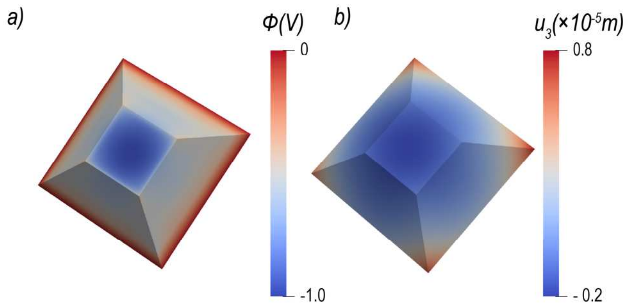

Figure 6: Distribution of (a) the electric potential φ and (b) the through-thickness mechanical displacement u_3 in the deformed configuration of the pyramid. The dimensions of the pyramids in the simulation are $a_1 = 1.13\ mm$, $a_2 = 2.72\ mm$, and $d = 0.76\ mm$ as defined in Figure 4.

The results shown in Figure 6 constitute a preliminary step and are shown in order to demonstrate the accuracy of the FE model. The effective piezoelectric charge coefficient is not competitive with PZT. However, this is largely a geometric effect, and with smaller pyramids, the effective charge coefficient should be dramatically higher (see Figure 5). As an example, a pyramid whose size has been decreased by a factor of 10 would have an effective piezoelectric charge coefficient that is 10 times higher (equation (4)). Numerical simulation also confirms these results. Simulating the same pyramid shown in Figure 6, but scaled down by a factor of 10, results in a voltage of -79.8V. The resulting effective piezoelectric charge coefficient is $54.9\ pC/N$, an increase of 9.15 times. It is worth noting here that the large effective piezoelectric charge coefficient for small pyramids could be misleading. Consider the coupling coefficient squared (k^2) that represents the amount of converted energy divided by the applied energy. For a piezoelectric material, $k_{33}^2 = \frac{d_{33}^2 c_{11}}{\chi}$. One might conclude that an increase 10X in the effective piezoelectric charge coefficient would result in a 10X in the coupling coefficient (k). However, as k cannot exceed 1, such a conclusion would clearly not be warranted. This indicates a need for a more comprehensive approach to evaluate the flexoelectric material performance. Furthermore, the simulation is for bulk flexoelectricity, not space charge flexoelectricity. Although a publicly available FE code to simulate bulk flexoelectricity is a needed contribution in its own right, we plan to extend this formulation to be able to accurately simulate the SCIF effect.

CONCLUSIONS

In this paper, we have demonstrated key building blocks to realize a new energy harvesting transduction technology, space charge induced flexoelectric (SCIF) transducers. These building blocks include an experimental demonstration of the effect by means of a doped silicon beam with HfO_2 insulating layers that showed a flexoelectric coefficient of 4.9 +/- 0.4 $\mu C m^{-1}$. Truncated pyramids can, in principle, generate much higher strain gradients, and thus larger flexoelectric polarizations, than bending beams. To this end we developed a computational platform that can model bulk flexoelectricity as a first step toward a full computational system to enable numerical studies of SCIF transducers and serve as design an optimization tool.

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