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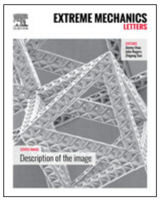

Pyro-paraelectricity

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ABSTRACT

The electrical responses of materials and devices subjected to thermal inputs, such as the Seebeck effect and pyroelectricity, are of great interest in thermal-electric energy conversion devices. Of particular interest are phenomena which exploit heterogeneities in the mechanics of heterostructured materials and systems for novel and unexplored thermal-electric responses. Here we introduce a new mechanism for converting thermal stimuli into electricity via structural heterogeneities, which we term "pyro-paraelectricity". Specifically, when a paraelectric material is grown on a substrate with a different lattice constant, the paraelectric layer experiences an inhomogeneous strain due to the lattice mismatch, establishing a strain gradient along the axis of the layer thickness. This strain gradient, induced via the lattice mismatch, can be multiple orders of magnitude higher than strain gradients in bulk materials imparted by mechanical bending (0.1 m^{-1}). Consequently, charge separation is induced in the paraelectric layer via flexoelectricity, leading to a polarization in proportion to the dielectric constant. The dielectric constant, and thus the polarization, in turn changes with temperature. Therefore, when a strained metal–insulator–metal (MIM) heterostructure is subjected to a thermal input, changes in the permittivity generate an electrical response. We demonstrate this concept of "pyro-paraelectricity" by employing a MIM heterostructure with a high permittivity sputtered barium strontium titanate (BST) film as the insulating layer in a platinum sandwich. The resulting strain gradient of more than $10^4\ \mathrm{m}^{-1}$ due to the structural heterogeneity was verified by an X-ray diffraction scan. To demonstrate "pyro-paraelectricity", the MIM heterostructure was subjected to a thermal input, thereby generating current which was highly correlated to the thermal input. A theoretical model was found to be consistent with the experimental data. These results prove the existence of "pyro-paraelectricity".

1. Introduction

The development of new methods to study the responses of materials and devices to thermal stimuli could enable new fundamental insights and applications in micro-robotics [1–4], thermal-electric generators [5–7], and biomedical sensors [8–11]. The thermal-electrical response is also important from an energy scavenging perspective, as 60% of energy currently produced from all sources in the United States is lost in the form of wasted heat [12]. Various fundamental mechanisms involving the electrical responses of materials and devices to thermal inputs have been well characterized, including the

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Seebeck effect [13,14], thermoelectricity [5–7], and pyroelectricity [8,9,15]. These mechanisms offer unique advantages including high reliability, environmental friendliness, and freedom from moving parts [6]. In addition, breakthroughs in thermal-electrical responses have been demonstrated over recent years, including the realization of flexible forms for wearable electronics [7], and novel thermoelectric phenomena in hierarchical material architectures [16] and high *ZT* values in nanomaterials [17–20]. However, methods exploiting heterogeneities in the compositions and mechanics of heterostructured materials, systems, and devices are relatively unexplored as a viable means for investigating thermal-electric responses.

Flexoelectricity is the generation of an electric polarization in an insulating solid subjected to a strain gradient. In contrast to piezoelectricity, which occurs only in crystal point groups without a center of symmetry, flexoelectricity can occur in all point groups. Yet, the flexoelectric effect is weaker than the piezoelectric effect due in part to the smaller flexoelectric coupling coefficients [21–23]. Further, due to mechanical restrictions, the maximum strain gradient introduced by external stress is on the order of 0.1 m^{-1} [24] in rigid bulk materials, further limiting the flexoelectric polarization inducible by external stress [21]. By contrast, a reasonable amount of uniform stress can be easily applied even to a rigid material, and the piezoelectric response is more easily measureable [22]. For instance, a maximum current of ∼50 pA was generated and measured under a ∼0.011 m^{-1} strain gradient in a bulk crystal of barium strontium titanate (BST) [25]. This magnitude of current is much lower than typical currents (100–500 nA) that can be generated via piezoelectricity [26–29].

Studies of flexoelectricity have mostly involved the properties of bulk materials, with very few reports on potential applications [25,30–33]. Advances in epitaxial engineering provide an alternative means of imposing significant strains and strain gradients in thin films. For example, by introducing a lattice mismatch of ∼1%, it has been shown that a large strain can be induced in a $SrTiO_3$ thin film deposited upon a $DyScO_3$ substrate, with the result that the $SrTiO_3$ was converted from a paraelectric state into a ferroelectric state by the significant stress induced via the lattice mismatch [34]. Epitaxial engineering has also been utilized to introduce large strain gradients in thin film systems. A previous study with ferroelectric $HoMnO_3$ showed that a large strain gradient (10^6 m^{-1}) can be induced via lattice mismatch, and the ferroelectric characteristics of the $HoMnO_3$ thin film can be tuned by a flexoelectricity-induced electric field [35]. Epitaxial engineering with flexoelectric systems can thus inspire new fundamental research directions in flexoelectricity.

Here, we demonstrate a new mechanism for converting thermal stimuli into electricity using such heterogeneous architectures, which we refer to as "pyro-paraelectricty". Specifically, a dielectric layer in a paraelectric state is first grown on a material of a different lattice constant. Due to the lattice mismatch, the dielectric layer undergoes an inhomogeneous strain due to the heterointerface [35–38]. As a result, a strain relaxation is established along the axis of the layer thickness. The strain gradient triggered by the lattice mismatch can reach 10^6 m^{-1}, more than six orders of magnitude larger than in bulk materials [24]. Since the dielectric layer is in a paraelectric state, the strain will not incur any piezoelectric polarization, simplifying interpretation of the measurement results. Nevertheless, the strain gradient does result in separation of charges in the dielectric layer via flexoelectricity, leading to a polarization.

Fig. 1 illustrates this concept in detail. Fig. 1(a) shows that when a flexoelectric material is grown upon a material of a different lattice constant, the lattice mismatch results in strain relaxation along the axis of thickness, forming a strain gradient and thus a flexoelectric polarization. A metal–insulator–metal (MIM) heterostructure sandwich containing the flexoelectric material as the insulator layer is a convenient form factor for measuring this polarization. Next, the dielectric constant of the dielectric layer is temperature-dependent, so the polarization changes with temperature as shown in Fig. 1(b). Since the polarization varies with temperature, when the MIM sandwich is subjected to a thermal input, changes in permittivity induced by the thermal input will lead to a measureable electrical response. A schematic of this mechanism is described in Fig. 1(c).

Specifically, we demonstrate this concept of "pyro-paraelectricity" by employing a MIM heterostructure containing a high-permittivity (dielectric constant ∼200), flexoelectric sputtered BST film as the insulating layer in a platinum sandwich. The MIM heterostructure was then subjected to a cycled thermal input. This led to the generation of a current which was highly correlated with the thermal input. Low-permittivity SiO_2 (dielectric constant ∼5) was used as a control, which showed a comparatively negligible electrical response under the same thermal input. A theoretical model was found to be consistent with the experimental data. These results prove this new effect, both experimentally and theoretically.

2. Fabrication and characterization of MIM heterostructure

A high-permittivity BST film ($Ba_xSr_{1-x}TiO_3$, $x = 0.625$) was chosen as the dielectric layer, since the polarization induced by flexoelectricity is proportional to the permittivity [39]. Dielectric materials exhibit their largest dielectric constants during the ferroelectric–paraelectric phase transition, as has been observed in both bulk materials [25] and thin films [40]. Therefore, the composition of BST was chosen such that the Curie temperature (∼0 °C, estimated from [41]) is below room temperature (20 °C), to ensure that the BST is paraelectric while achieving a high dielectric constant. The MIM heterostructure fabrication process began by sputtering Pt on a thermally-grown oxide (∼300 nm) on a silicon wafer (University Wafers, Boston, MA), followed by post-annealing at 800 °C in air to improve Pt adhesion to SiO_2. A 150 nm BST film (stoichiometric $Ba_{0.63}Sr_{0.37}TiO_3$ target purchased from ACI Alloys Inc, San Jose, CA) was then RF sputter-deposited on the Pt/SiO_2 wafer, followed by post-annealing at 700 °C in Ar. Finally, a 100 nm Pt top electrode of area 500×500 μm^2 was electron-beam evaporated on the BST through a shadow mask. A schematic of the final MIM structure is shown in Fig. 2(a).