

## Simulation and ultrasonic study on domain processes in ferroelectrics

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Ferroelectric systems usually contain many different polarization domain states that couple strongly with elastic strain. These domains will co-exist and form complex structures, for example, the  $90^\circ$  twins in a tetragonal ferroelectric system. Theoretically speaking, during the polarization reversal process in a single crystal, domains whose polarization axis is different from that of the applied field could appear. However, textbook mechanism for polarization reversal did not include polarization rotation. It was described as a three-step process: reversed polarization domain nucleation, forward growth, and sideways growth of the reversed polarization state. Optical microscopy cannot see these domain switching processes since the mini-domain mixture will appear uniform to the visible light. In addition, some materials may not even be optically transparent. TEM, on the other hand, will destroy the 3D nature of the ferroelectrics and the boundary constraints often confine the switching process. Recently, we have performed a computer simulation as well as innovative measurements of the domain processes using ultrasonic technique. The simulation results of a 2D four variant model show that the switching path is not as given in the textbook. Instead, two consecutive  $90^\circ$  domain switching occurred. In order to verify this phenomena, we have monitored the polarization reversal process using ultrasound in a single crystal  $0.955\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{--}0.045\text{PbTiO}_3$  which has a rhombohedral 3m symmetry. Direct evidence indicates that the polarization reversal in this system is via a path involves two consecutive domain switching processes, i.e.,  $0^\circ \rightarrow 71^\circ \rightarrow 180^\circ$ , instead of the textbook mechanism of  $0^\circ \rightarrow 180^\circ$  domain switching. Our results revealed the intrinsic nature of fatigue in some ferroelectrics in which the reversal process involves large elastic deformation.

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## Piezoelectric microactuator arrays using composite PZT thick films

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Preparing crack-free lead zirconate titanate (PZT) films with thickness up to  $50\text{ }\mu\text{m}$  is still a challenge for ferroelectric MEMS applications. In this paper, a modified 0–3 composite route for thick film preparation has been reported. The film properties such as microstructure, crystallinity, ferroelectric, and dielectric properties have been optimized in terms of the variable processing parameters such as concentration of the sol–gel solution, powder/solution mass ratio, vehicle content, annealing temperature, powder size, and cold isostatic pressing. Within the optimum processing conditions, the thickness of crack-free PZT films on the platinum-coated silicon substrates can be easily adjusted between 1 and  $50\text{ }\mu\text{m}$ . PZT/silicon diaphragm array with such composite thick films has been fabricated by using silicon micromachining. The electromechanical properties of the diaphragms have also been evaluated and presented.

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## Novel high-pressure crystallization process for the preparation of electronic ceramic thin films at low temperatures

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The research and development of thin-film technology for electronic ceramics has been stimulated by the necessity for producing microelectronic devices and systems having compact size, light weight, and low power consumption. Electronic ceramic thin films are being extensively applied in various types of electronic and optical devices such as microelectromechanical systems, dielectric capacitors, sensors, and electro-optic displays.

Because the electronic ceramic thin films are difficult to be crystallized, either in situ heating or post-annealing high temperatures for complete crystallization is necessary. In order to reduce the crystallization temperature of electronic ceramic thin films, a novel high-pressure crystallization (HPC) process has been developed. The crystallization temperatures of ceramic thin films (PZT and  $\text{Ta}_2\text{O}_5$ ) were significantly decreased to lower than  $400^\circ\text{C}$ . It was found that the crystallization process of ceramic thin films was markedly enhanced by high-pressure processing. In addition, the interactions between ceramic films and substrates were substantially reduced. The formation process and development of the microstructure were investigated by XRD, GIXD, SEM, and SIMS. The prepared thin films were demonstrated to exhibit high dielectric constants and good electric properties. This HPC approach for synthesizing electronic ceramic thin films can effectively reduce the thermal budget and alleviate the malfunctions resulting from pronounced interdiffusion

of the substrate species into the films. The developed novel process can be utilized for integration of electronic ceramic films with ULSI technology in designing new generation semiconductor devices.

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### Epitaxial metal oxide thin film heterostructures for tunable chemical sensors

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Thin film sensors based on oxide heterostructures have an advantage over conventional chemical sensors in terms of lower cost, lower power consumption, lower weight, and faster response. In this paper, we present our recent studies on the epitaxial SnO<sub>2</sub>/TiO<sub>2</sub> and SnO<sub>2</sub>/Cr<sub>2</sub>O<sub>3</sub> heterostructures deposited on the sapphire and TiO<sub>2</sub> substrates by a femtosecond pulsed laser deposition. We have successfully synthesized epitaxial oxide heterostructures consisting of p–n junctions. It was found that the electrical properties and gas sensitivities of the epitaxial heterostructures can be tuned by chemical doping in oxide and by electrical bias across the p–n junctions. We also found that the electrical transport properties of semiconductive oxide multilayers strongly depend on the layer thickness and the structure of the heterojunctions. This study suggests that epitaxial metal oxide heterostructures with p–n junctions could make a new avenue for the development of selective, tunable chemical sensors.

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### Control of microporous structure for semiconductor gas sensor

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Oxide semiconductor gas sensors detect a target gas (analyte) from a change in electrical resistance. Thanks to extensive R&D effort to date, this type of sensor has grown to be produced in a massive scale for various applications such as gas leakage alarms, CO detectors, breath checkers, auto dampers, alcohol checkers and so on. Yet, there are many kinds of gases else, which are desired to be targeted

for sensor detection, including volatile organic compounds (VOCs), endocrine disrupting chemicals (EDCs), and bio- or food-related various gases. Most of these gases are present at small concentrations, so that the relevant sensors are required to have very high sensitivity. High-sensitivity design seems to be one of the most urgent research subjects for semiconductor gas sensors.

From a basic viewpoint, it has been recognized that the receptor function of this type of sensor is provided by the surface of oxide grains or a foreign substance (sensitizer) dispersed on them, while the transducer function is by the grain boundaries. However, this scheme ignores microstructure of polycrystalline devices except that it predicts that unusual situation arises when the grain size becomes smaller than twice the thickness of the surface space charge layer of grains. The importance of microstructure or microporous structure is made evident when one considers that gaseous molecules diffuse in the polycrystalline device, while if inflammable, they are consumed by the reaction with the surface oxygen of the grains. Based on a simple diffusion–reaction equation, sensor response (sensitivity) at steady state for a thin film device can be formulated under simplifying assumptions to be linear to  $(1/m) \tanh m$ , where  $m = L(k/D_k)^{1/2}$  and  $L$  is the film thickness,  $k$  the first order reaction rate constant and  $D_k$  Knudsen diffusion constant. Thus,  $S$  becomes larger when  $m$  is small ( $<1$ ), or, in other words, when the device has open structure (large  $D_k$  and small  $L$ ). The control of microporous structure is therefore decisively important for designing a high sensitivity sensor, beside exploration for sensitizers. Some examples of recent studies will be introduced to demonstrate the importance of microporous structure control.

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### Bio-inspired processing of electroceramic thin films and micropatterning

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There has been a growing interest recently in “bio-inspired” or “bio-mimetic” approaches to prepare ceramic thin films at ambient temperatures in solutions, as they are expected to enable us to develop novel processing methods and manufacturing processes that are low cost and environment-friendly. Conventional lithography technology is facing many problems, and alternative novel technology is intensely required to overcome the present issues and to better match the future nanotechnology. Bio-inspired processing