Piezoresponse Force Microscopy

Application Note

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This application note presents a primer on the direct and reverse piezoelectric effects and their uses, and the instrumentation and applications of piezoresponse force microscopy.

Piezoelectricity

The Greek word "piezo" means pressure. In 1880, the brothers Jacques and Pierre Curie (18 and 21 years old!) reported on a discovery that the following year W. G. Hankel called piezoelectricity, a descriptive name for the phenomenon, in which mechanical stress applied to a sample of some materials apparently creates electric charge on certain surfaces of the sample.[1,2] The total charge of the sample remains unchanged by the piezoelectric effect, but as a result of the mechanical stress, surface charge density is created.[3] If a conductive material covers the charged area, and a conductive path exists from there to an electrometer, a charge of equal in magnitude registers in the electrometer, but that charge belongs to the conductors, not the sample.

Direct and Reverse Piezoelectric Effects

The origin of piezoelectrically induced polarization surface charge can be traced down to the changes on the nanometer scale in the orientation of electric dipole moments in the material. Some surfaces of the material accumulate excess positive bound charge and some negative. This phenomenon is called the direct piezoelectric effect.

The reverse piezoelectric effect is the term given to the phenomenon in which an applied electric field produces a mechanical strain in the same materials, the piezoelectric materials. The reverse piezoelectric effect was first predicted by Lippmann, and shortly afterwards demonstrated experimentally by Jacques and Pierre Curie.[4]

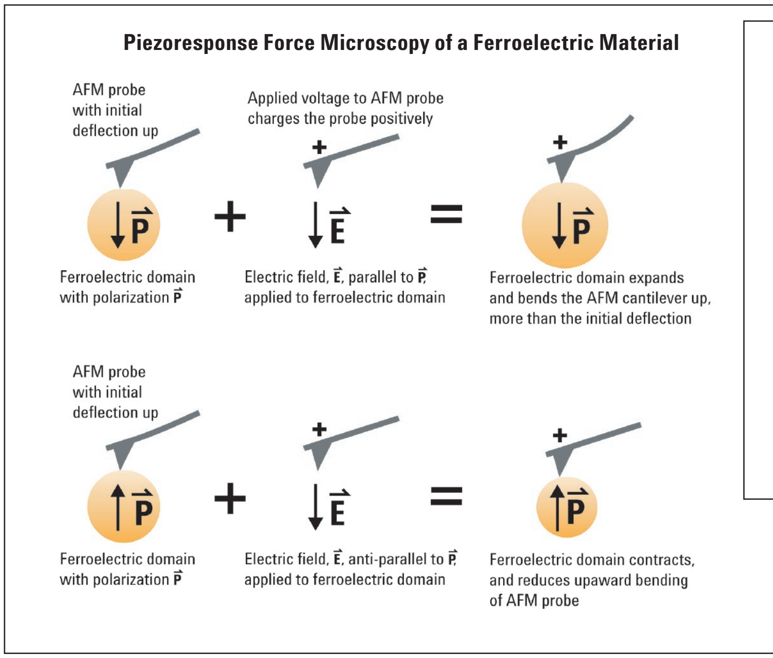
Applications of Piezoelectricity

Piezoelectric materials have had wide-ranging applications for many decades. In the 1960s and 1970s, manufacturers of piezoelectric ceramics, for example, were offering products with different performance characteristics, for very diverse applications. For example, large mechanical response and low losses for applications in ultrasonics, sonar, and ignition; high coupling coefficients and charge constants, for applications in sensors; slow aging of dielectric permittivity and high temperature stability for phase-sensitive applications such as in ultrasonic delay lines for color television receivers.[m]

More recently, with accelerated progress in miniaturization and technological infrastructure built around microtechnology, the sphere of applications for piezoelectric materials has grown enormously. Since piezoelectricity converts two different forms of energy (mechanical and electrical) that play important roles in microtechnology, piezoelectric transducers are now ubiquitous in all kinds of products, ranging from relatively mundane household appliances,and consumer product appliances, to more advanced consumer products, to sophisticated scientific instruments and industrial tools.

Basically, there has always been two important categories of applications: sensors, and actuators. The direct piezoelectric effect is used almost exclusively in sensors, for measuring force, torque, acceleration, pressure, strain; the notable exception to this is their use in voltage generators for creating sparks and igniters. The reverse piezoelectric effect is used mainly in two ways: the resonant mode and the non-resonant mode. The non-resonant mode is used for actuation and positioning, for example in inkjet printers and in piezoelectric motors. Resonant applications include not only actuators, e.g., generating (surface and bulk) acoustic waves and ultrasonic waves, but also resonant sensors, in which the resonance frequency of the piezoelectric sensing element changes as this element interacts with the measurand. The resonant mode also has time and frequency applications in electronics, in filters, and oscillators.

One example where the direct and reverse piezoelectric effects are both used (as sensor and actuator) in key elements of the same technology, is in some atomic force microscopes (AFM), where the raster-scanning is performed with piezoelectric actuators, as is the actuation of the micro cantilever in



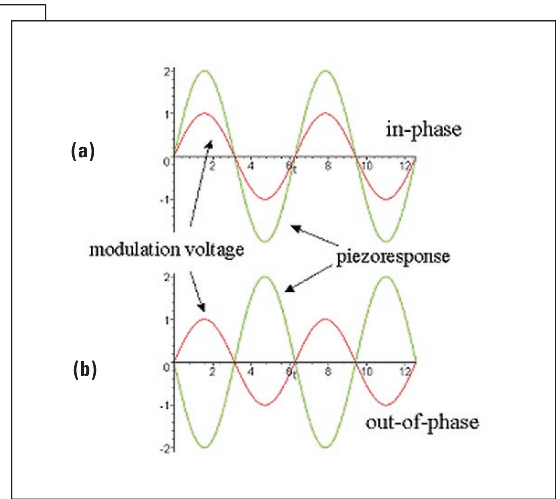


Figure 1. (a) In-phase and (b) out-of-phase piezoresponse of a ferroelectric material to an applied electric field result from the polarization being respectively parallel and anti-parallel to the applied field.[19]

feedback; the cantilever deflection is measured using a thin film of piezoelectric material. This material is deposited on the AFM cantilever itself and its response is measured piezoresistively.[6,7]

Another example is where acoustic waves are generated by applying a modulating electric field to piezoelectric elements, and then detected by other piezo-elements (piezoresistive sensors) a short distance away, in which distance the traveling acoustic wave interacts with the measurand, and this interaction alters the characteristics of the wave as received by the piezoresistive sensor.[8]

Basic Mathematical Formulation of Piezoelectricity

The direct piezoelectric effect is in the simplest approximation described by a linear relation between the mechanical stress, X, and the resulting polarization charge density, P:

$$P = d \; . \; X,$$

Where d is called the piezoelectric strain coefficient (the nomenclature becomes clear in the definition of the reverse piezoelectric effect.) The dimensions of d in the SI are Coulomb per Newton (C/N).

In the reverse piezoelectric effect, the relationship between the applied electric field, E, and the ensuing mechanical strain, S, is in the simplest approximation, again, linear:

$$S = d \; . \; E,$$

which makes clear the choice of the name for the constant d.[9]

All Ferroelectrics are also piezoelectric. For a ferroelectric material, when an electric field is applied to the sample, the material expands if the field is parallel to the material's polarization, and contracts if anti-parallel. People usually call this property of a (ferroelectric) material its *piezoresponse*.[10] When a small ac modulation is added to the applied field, the piezoresponse also oscillates, in-phase with the modulating field if the polarization is parallel to the field, and out-of-phase if anti-parallel (Figure 1.) This is how piezoresponse force microscopy works, as we will discuss next.

Piezoresponse Force Microscopy

Piezoresponse Force Microscopy (PFM) is a scanning probe microscopy (SPM) technique based on the reverse piezoelectric effect, where a (piezoelectric) material expands or contracts upon applying to it an electric field.[11]

PFM is an Imaging Technique. In the classification of Imaging Techniques, it falls under Derivative Imaging Modes. It is a derivative of the Primary Imaging Mode called Contact Mode AFM. In PFM, the AFM probes a sample's mechanical response to an applied electric field. The AFM tip used in PFM is usually made of, or is coated with, a conductive material, as this conductivity enhances the electrical contact between the tip and the sample. An ac modulation with an optional dc offset bias is applied to the tip, which is in contact with the sample surface, and the piezoresponse of the sample is measured from the deflection of the AFM cantilever. This measurement uses a lock-in amplifier (Figure 2). The frequency of the applied ac voltage is typically far from (below) the fundamental resonance frequency of the AFM cantilever so as to avoid driving the cantilever into resonant oscillations.[12]

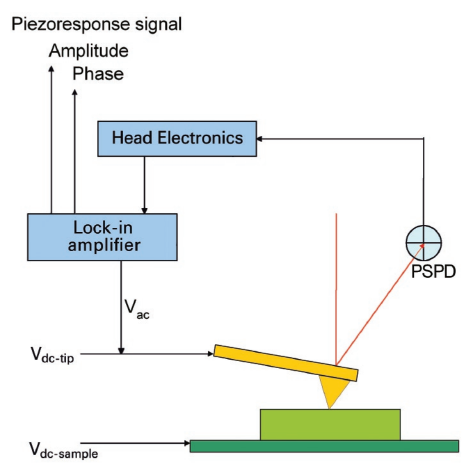


Figure 2. A typical experimental setup for PFM involves lock-in detection and optional dc offsets to the sample and the tip. (PSPD: Position Sensitive Photodetector.)

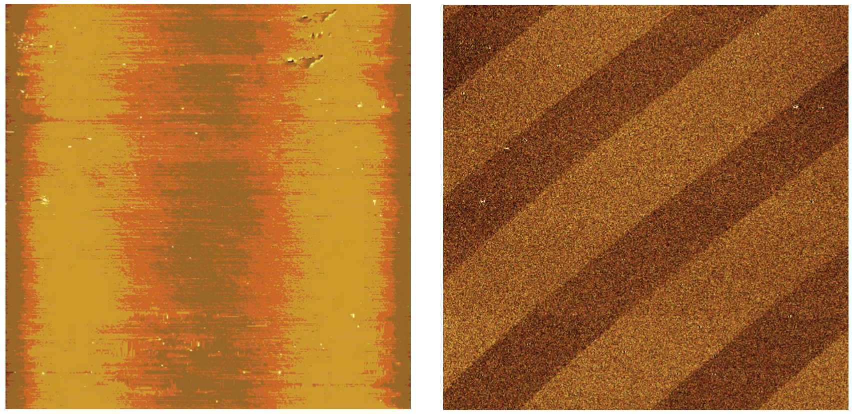


Figure 3. Contact Mode Topography image (left) and PFM Phase image (right) of a region of a Lithium Niobate sample. The PFM image clearly identifies regions with different polarization states.

The Utility of PFM

To intelligently design and efficiently manufacture piezoelectric-based transducers for specific applications in micro- and nano-technology, it is necessary to understand the piezoelectric properties of the transducer's functional element, at the level of its building blocks, that is to say, at or near the molecular level. PFM is one of the most important tools that enables measurements and characterization of piezoelectric behavior of materials on the nanometer, and sub-nanometer scale. There is currently no other tool currently available that can routinely and with the same ease measure the electromechanical response of a material on the level of individual nanometer-scale grains. The PFM has been shown to delineate regions of different piezoresponse with sub-nanometer lateral resolution.[13]

In Figure 3, the PFM image (phase signal, right image) shows contrast that delineates regions of differing piezoresponse on the surface of a Lithium Niobate sample, whose topography (left image) reveals no features corresponding to those in the piezoresponse image. The PFM signal in this image is recorded from the vertical movement of the AFM tip, but similarly, the lateral movement of the tip may be recorded (as in Lateral Force Microscopy) to construct a map that is descriptive of in-plane polarization of the various regions on the sample surface.

PFM has already proved uniquely useful in investigating the nanometer-scale piezoelectric properties of ferroelectrics. Ferroelectric thin films are the subject of intense research and development for their optoelectronic, sensor, and especially high-density memory applications. Since all ferroelectrics are also piezoelectric, much can be learned about the ferroelectric properties, including piezoresponse. The lateral resolution of PFM provides highly localized information about the electromechanical behavior of thin ferroelectric films (Figure 4).

For example, as thin films of ferroelectric materials are grown from isolated islands on metal substrates (e.g., for high-density memory applications), one key question to be answered is, at what point during the growth of the thin film is ferroelectricity present. To this end, the PFM can be used to interrogate a given nanometer-scale domain in an island for its piezoelectric response; if there is a piezo response, this implies ferroelectricity.[14]

PFM Spectroscopy is a non-imaging technique that compliments PFM imaging. In PFM Spectroscopy, the piezoresponse of a given location on the sample can be mapped versus, for example, the dc bias ($V_{dc\text{-}tip}$, Figure 2), or the frequency of the ac signal (V_{ac}, Figure 2) applied to the sample via the tip. This technique can also be used to study hysteretic characteristics of the piezoresponse.[15,16]

Summary

The piezoelectric effects, reverse and direct, are now known to be present in materials that belong to a wide range of material groups, including polymers, biomaterials[17], wood[18], ceramics, and non-metallic crystalline solids whose crystal structure has no symmetric center.

With the growing interest in the utility of piezoelectricity and its many manifestations on the nanometer scale, Piezoresponse Force Microscopy has become recognized as a key tool in advancing the research and development of applications based on piezoelectric materials in general, and and the industrially important ferroelectrics.

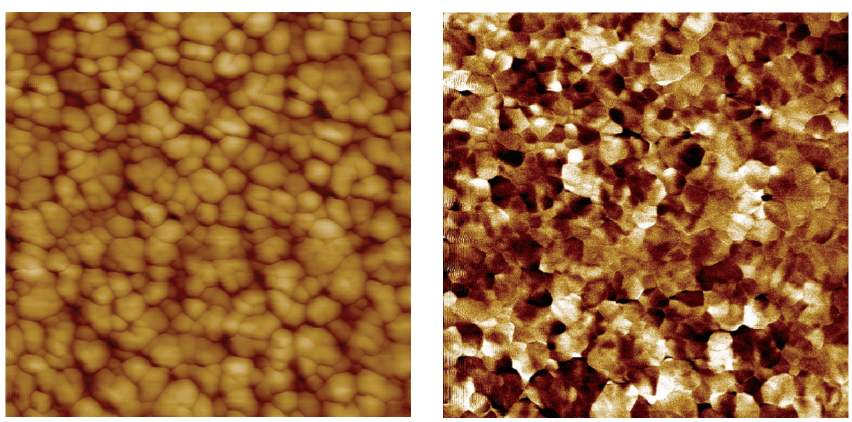


Figure 4. Contact Mode Topography image (left) and PFM Phase image (right) of domains on a thin film of ferroelectric (courtesy Louis Pacheco, Scientec, Fr.)

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7. Piezoresistive sensors are based on the piezoelectric effect, but work differently from piezoelectric sensors. In piezoelectric sensors, what is detected is the induced polarization charge that comes about due to the mechanical stress. This method does not require a power supply, and for this reason a piezoelectric sensor categorizes as an active sensor. In piezoresistive sensors, by contrast, the electrical resistance of a biased piezoelectric element (usually a thin film) is detected as the measurand interacts with that element and changes its electrical resistance. Piezoresistive sensors are passive sensors, requiring an external source of power. Zinc oxide (ZnO) is frequently used for its piezoresistive response.
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10. Piezoresponse Force Microscopy (PFM) was initially developed to investigate ferroelectric materials. In fact, the term piezoresponse as described here (and PFM) appear to be intimately associated with the term ferroelectric in the great majority of published literature so far. Since piezoelectricity is not restricted to ferroelectrics, however, PFM is finding applications beyond ferroelectrics. Although the loose definition of the word piezoresponse does not apply to non-ferroelectrics, PFM is now used to include AFM-based investigation of nanometer-scale electromechanical response of any material to an applied voltage.
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