## Nanoscale Visualization and Control of Ferroelectric Domains by Atomic Force Microscopy

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The nanoscale visualization and control of domain structure with atomic force microscopy (AFM) in the ferroelectric crystal guanidinium aluminum sulfate hexahydrate is reported. The origin of the domain contrast in the topographic of AFM images is explained by the piezoelectric deformation of the crystal surface in the internal electric field. The domain structure was modified by applying a voltage to the conductive AFM tip. The dynamics of domain growth has been directly observed for the first time with a resolution of 10 nm.

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One of the main features of ferroelectrics which singles them out among other materials is the possibility of changing the direction of spontaneous polarization under an applied electric field. Over the past few years, interest in ferroelectrics has essentially increased as a result of recent achievements in the processing of ferroelectric thin films and their wide application in various electronic and optoelectronic devices. Recently the possibility of imaging ferroelectric domains with atomic force microscopy (AFM) [1,2] in the micron range has been reported [3,4]. AFM could be a powerful tool for the nanoscale study of domain structure, but a lack of understanding of the origin of ferroelectric domain contrast in AFM obscures the image interpretation. An attractive prospect for AFM, but not yet realized, would be direct nanoscale imaging of domains during their switching. This would allow one to directly study the nature of ferroelectric behavior.

In the present paper an analysis of the basics of ferroelectric domain contrast during contact (repelling force) AFM imaging is given. Using a conductive cantilever under variable electric potential, a controllable local switching of polarization in the ferroelectric crystal was realized and the dynamics of domain nucleation, growth, and interaction was studied with nanoscale resolution.

To investigate the domain contrast in AFM we used a guanidinium aluminum sulfate hexahydrate (GASH) crystal, chemical formula  $C(NH_2)_3Al(SO_4)_2 \cdot 6H_2O$ . GASH is a uniaxial ferroelectric, belonging to the trigonal crystal system (space group P31m) [5]. The spontaneous polarization  $P_s$  is about 0.35  $\mu$ C/cm², the dielectric constant  $\varepsilon_c$  along the polar axis is 15, and the coercive field is about 1.5 × 10<sup>5</sup> V/m [5]. GASH has a perfect cleavage plane normal to the polar axis  $\varepsilon$ , which is quite suitable for studying the domain structure. It has been studied using various techniques, among them scanning electron microscopy [6], powder deposition [7], pyroelectric probe

imaging [8], nematic liquid crystals [9], and, recently, by AFM with micrometer resolution [3,4].

The crystal plates, which were cleaved in air, were about 0.3 mm thick. They were investigated in an ambient environment using a Nanoscope III scanning probe microscope operating in AFM topography and friction modes. To distinguish the contrast associated with topography from that related to electrostatic tip charging, we used two types of cantilevers—a standard one with a nonconductive  $\mathrm{Si}_3\mathrm{N}_4$  tip and a gold-coated conductive tip and cantilever. Both cantilevers had a rigidity of 0.09 N/m and tips with a curvature radius R of about 100 nm. During imaging with the conductive tip we applied a dc potential V of up to  $\pm 5$  V to the bottom electrode, whereas the tip was held to zero potential.

The AFM images of the GASH surface showed monatomic cleavage steps of about 0.8 nm in height and of 1-10  $\mu$ m in separation. The well known GASH domain structure in the form of rows of cylindrical domains [10] together with a configuration consisting of domains of one sign embedded into the larger domain of opposite sign [Fig. 1(a)] was observed in the topography image. The domains appeared as circular protrusions or depressions with a 100-500 nm diameter and a 10-50 nm height. There was an attempt to associate the domain contrast in AFM with the electrostatic interaction between polarization and tip charges [4]. Such an explanation is reasonable for the noncontact mode [3] where the conductive tip, biased by electric potential, is easily deflected by the stray electric field of the domain. Nevertheless, in a contact mode, a tip-surface distance is almost fixed due to the strong short-range tip-surface repulsive interaction, resulting in imaging of mainly the surface topography. Moreover, there was no essential difference in the topography contrast observed for the nonconductive cantilever and the electrically grounded