

Electrostatic force microscopy on ferroelectric crystals in inert gas atmosphere

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An electrostatic force microscope operated in inert gas atmosphere has been used to investigate the domain structure of ferroelectric crystals. The electrostatic force observed in the inert gas atmosphere is compared to that measured under ambient conditions. The domain structure of guanidinium aluminum sulfate hexahydrate has been revealed in the dynamic as well as in the static noncontact operation mode of the electrostatic force microscope. We have studied the dependence of the domain contrast on the applied external electric field in the inert gas chamber and under ambient conditions. The sign of the domain polarity could be identified in the static operation mode of our microscope. [S0163-1829(97)04601-8]

I. Introduction. Ferroelectric crystals have been a subject of growing interest in the last years due to the existence of a wide variety of applications in, e.g., laser optics and data storage devices.¹ Among the dielectric materials, ferroelectrics show a nonzero spontaneous polarization \mathbf{P}_s in the absence of an external electric field below the Curie temperature.² Surfaces of a ferroelectric crystal possess an electric charge which is proportional to the perpendicular portion of \mathbf{P}_s on the respective face of a crystal. The resulting electric field outside the crystal is reduced by the formation of a domain structure in the crystal. Neighboring domains show different orientations of \mathbf{P}_s . The domain structure of a ferroelectric crystal is a characteristic feature and therefore of great interest for basic research and applications. Nowadays, strong effort is made to produce regular arrays of domains in strong ferroelectrics, such as lithium niobate, for the use in, e.g., second-harmonic generation.³

The ferroelectric domain structure can be imaged by a variety of techniques as, e.g., scanning electron microscopy,^{4,5} optical microscopy,⁶ and transmission electron microscopy using a decoration technique.⁷ Recently, it has been demonstrated that electrostatic force microscopy (EFM) is able to map the domain structure of ferroelectric crystals with 50 nm lateral resolution.⁸⁻¹⁰ EFM has the advantage over other techniques that the magnitude and the distribution of the electric field and field gradient in the vicinity of the surface can be imaged.

When a ferroelectric crystal is kept under ambient conditions, then it attracts charged particles from the environment. These charges can considerably alter the domain structure of the crystal since the energetically favorable status of a crystal with completely compensated surface charges is the single domain state. On the other hand, surfaces of many ferroelectric crystals are etched by the thin water layer which is present on the crystal faces under ambient conditions.^{9,11,12} However, until now all EFM investigations of the domain structure of ferroelectrics have been carried out under ambient conditions.

In the present work, we show first results of EFM investigations of the domain structure of ferroelectric guanidinium aluminum sulfate hexahydrate (GASH) crystals obtained in the inert argon atmosphere. Inert argon conditions guarantee a water and charge-carrier free environment. Therefore, when the sample is cleaved within the inert argon chamber etching of surfaces and compensation of surface charges can be excluded in these experiment.

II. Experimental. GASH [chemical formula $C(NH_2)_3Al(SO_4)_2 \cdot 6H_2O$] crystals were grown from aqueous solution at a temperature of 46 °C. The lattice constants of the hexagonal unit cell are $a = 1.174$ nm and $c = 0.895$ nm.¹³ The spontaneous polarization is oriented parallel to the c axis and has a value of $0.35 \mu C/cm^2$ at 20 °C.¹³ The GASH crystals can be easily cleaved parallel to the (0001) plane. The samples were glued using silver paste onto metallic holders.

The EFM investigations have been performed using a commercially available instrument.¹⁴ In EFM a probe tip which is mounted on a cantilever-type spring is brought into close vicinity or even contact to the sample surface. The force interaction between the tip and a sample causes the cantilever to deflect according to Hooke's law.¹⁵ In our measurements, the topography and the electrostatic force have been detected independently of each other in two steps: First, the tip tracks one scan line in contact with the sample's surface. Afterwards, the tip is raised to a predetermined height above the surface and scanned along the path parallel to the previously stored scan line. The tip-sample separation is kept constant during the second scan. The deflection of the cantilever due to the electrostatic interaction between the sample and the tip is then plotted as a function of position. This procedure allows the simultaneous measurement of the topography and the electrostatic force and is called here the static operation mode.

The dynamic operation mode is sensitive to the force gradient.¹⁶ The cantilever is then oscillated close to its resonance frequency. The force gradient which arises from the

sample stray field causes a shift of the resonance frequency, which subsequently is determined by measuring the phase lag between the oscillation of the excitation piezo and the oscillation of the cantilever itself. For a simultaneous determination of the sample's topography and the electrostatic force gradient the EFM experiments using the dynamic operation mode of the microscope have been also performed in two steps, as described above for the static operation mode.

In order to maintain a stable electrostatic interaction between the EFM tip and a sample and to allow the application of an external voltage between the tip and a sample, cantilevers have to be conductive. In the dynamic mode, silicon cantilevers with a force constant of about 40 N/m and resonance frequencies from 300 to 330 kHz have been used. The silicon cantilevers are *n* doped and have a resistance of 0.01 . . . 0.02 Ω cm,¹⁷ which enables good conductivity without further treatment. For the measurements in the static operation mode, Si₃N₄ cantilevers with a spring constant of 0.6 N/m have been used.¹⁴ The cantilevers have been coated with a 15 nm thick gold layer on the tip side which secured a stable electric contact to the cantilever holder.

During the measurement, the tip has always been kept on ground potential. The maximum voltage of ± 12 V has been applied between a sample holder and a tip.

The microscope was housed in the inert argon gas chamber throughout the measurements. The oxygen as well as the water concentration was below 1 ppm. All samples have been cleaved in the argon chamber and therefore surfaces were practically free of water. In order to carry on comparative studies, the sample has been imaged first in the argon chamber and afterwards scanned under ambient conditions.

III. Results and discussions. The force acting on the tip is expected to vary for measurements in different environments. Therefore, force vs distance curves measured in argon atmosphere and under ambient conditions have been compared to each other. Highly oriented pyrolytic graphite (HOPG) has been chosen as a test sample, since charge distribution or conductivity of the HOPG (0001) surface show no tendency to vary laterally which could influence the results. HOPG has been freshly cleaved in the argon chamber to guarantee a clean and a water-free surface. After the acquisition of a force vs distance curve in argon atmosphere, the microscope and a sample have been taken out of the argon chamber, and the experiments have been repeated under ambient conditions. Both measurements have been performed using identical scan parameters and the same gold-coated Si₃N₄ tip. Figure 1 shows the comparison of typical force vs distance curves acquired in argon and in air.

When the tip is approaching the surface in air [line 1 \rightarrow 2 in Fig. 1(a)], it has no considerable interaction with the sample at the tip-sample separation of 1 μ m down to some nanometer above the sample. Close to the surface, the tip is strongly attracted due to both van der Waals force and meniscus force (point 3). The latter results from the existence of a contamination layer on the sample in ambient conditions. This contamination layer consists of, e.g., adsorbed water molecules and hydrocarbon compounds. By comparison, in argon atmosphere an attractive force acting on the cantilever is already visible several hundreds of nanometers above the surface. This can be concluded from the bending of the respective approach curve [line 1 \rightarrow 2 in Fig. 1(b)]. Addition-

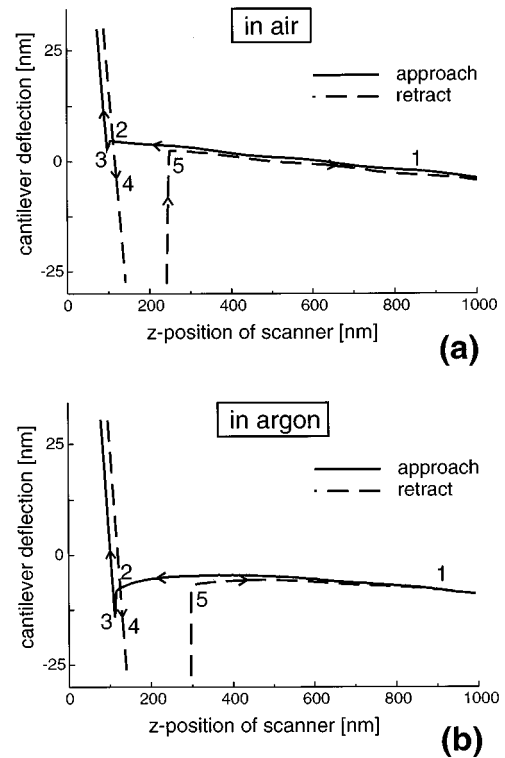


FIG. 1. Comparison of force vs distance curves measured (a) under ambient conditions and (b) in argon. Both curves were taken on HOPG (0001) using a gold-coated silicon nitride cantilever ($k=0.6$ N/m). No external electric field was applied. The stronger electrostatic interaction measured in argon compared to the one in air is visible in the bending of the approach and retract curves already several hundreds of nanometers away from the sample surface.

ally, the snap-in peak close to the sample surface (point 3) is much larger than the one observed during the measurements in air. When the tip is retracted, a hysteresis occurs due to the adhesive force between a tip and a sample surface [line 4 \rightarrow 5 in Figs. 1(a) and 1(b)]. The adhesion is stronger in the argon environment than in air.

The bending of lift curves representing either approach or withdrawal of the tip from the surface measured in argon atmosphere is a sign for the existence of a long-range electrostatic interaction between a tip and a sample, even though both have been held at ground potential throughout this experiment. In order to clarify this behavior, the electrostatic force between a gold-coated Si₃N₄ tip and a HOPG surface has been determined as a function of an external voltage applied between a sample holder and a tip both in air and in argon. The force has been calculated from force vs distance curve by measuring the difference in the deflection of the cantilever at two fixed z positions of the piezoscanner above the sample surface.

The electrostatic force on the tip is expected to show a parabolic dependence on the applied bias voltage.¹⁸ In our experiments, two contributions to the electrostatic force have to be considered: First, it is a capacitive term $1/2U^2(\delta C/\delta z)$ which describes the dependence of the electrostatic force on the externally applied voltage U and the tip-sample holder capacity C . The applied voltage induces a charge $Q_e = CU$ in the tip.¹⁸ The second term is due to a

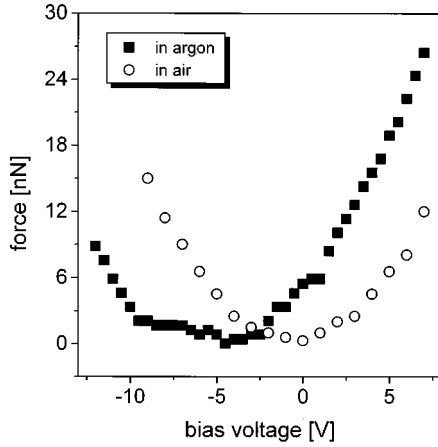


FIG. 2. Comparison of the electrostatic force as a function of bias voltage measured in argon and in air. The curves were taken on HOPG (0001) using a gold-coated silicon nitride cantilever with $k=0.6$ N/m. The force was determined from the approach part of force-distance curves as shown in Fig. 1 by measuring the difference in the cantilever deflection at two fixed positions of the piezo-scanner. The minimum of the electrostatic force in argon is found at a bias voltage of -5 V, whereas in air the minimum is about at zero external potential.

surface charge Q_s on the sample which induces an equal but opposite image charge within the tip. Finally, the total charge in the tip becomes $Q_t = -(Q_s + Q_e)$.¹⁸ The total electrostatic force acting on the tip can then be written as

$$\begin{aligned}
 F &= F_{\text{capacitive}} + F_{\text{Coulomb}} \\
 &\approx \frac{U^2}{2} \frac{\partial C}{\partial z} + \frac{Q_s Q_t}{4\pi\epsilon_0\epsilon_r z^2} \\
 &= \frac{U^2}{2} \frac{\partial C}{\partial z} - \frac{Q_s^2}{4\pi\epsilon_0\epsilon_r z^2} - \frac{Q_s C U}{4\pi\epsilon_0\epsilon_r z^2}, \quad (1)
 \end{aligned}$$

where z is the tip-to-sample distance during the lift scan. ϵ_r describes the dielectric constant of the materials between sample holder and tip. Equation (1) is a parabolic function of U . In the absence of any permanent charge in the tip or at the sample surface, the electrostatic force depends only on the capacitive term and is vanishing at zero external potential.

Figure 2 shows the dependence of the electrostatic force on the cantilever as a function of the externally applied voltage. Under ambient conditions, the electrostatic force has its minimum at a voltage of -0.5 V, where the $(-)$ sign is attributed to the polarity on the sample. The force shows the expected parabolic dependence on the voltage. For the measurements performed in argon, the $F(U)$ curve reveals also a parabolic behavior, but the minimum force is observed at a voltage of about -5 V.

According to Eq. (1), the relative shift of the minimum of the $F(U)$ curve along the U axis (Fig. 2) is attributed to the Coulomb interaction of a charge on the tip with its image charge in the sample. The results shown in Fig. 2 are independent of the electronic properties of the sample. The values for the minimum electrostatic force in air and in argon could have been verified additionally on such different samples as mica and GASH. The electrostatic force mea-

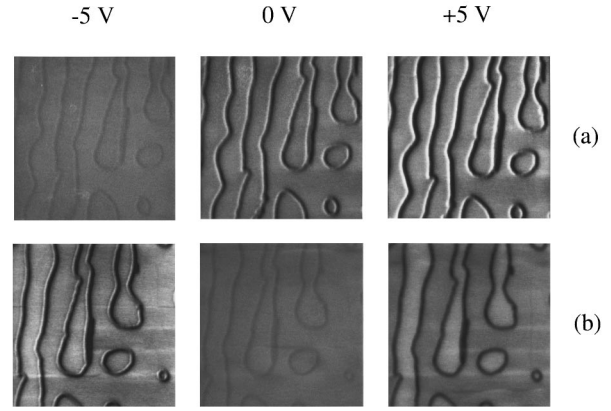


FIG. 3. Domain walls visualized in the dynamic operation mode on GASH (0001). The surface is smooth. All images show the lift mode scans at a nominal tip-to-sample distance of 60 nm. The silicon cantilever had the resonance frequency of 325 kHz. The image size is $30 \times 30 \mu\text{m}^2$. (a) Results of the experiments performed in argon atmosphere. The domain walls appear as lines. No contribution of the domains to the electrostatic contrast can be observed. The domain-wall contrast is the weakest at a bias of -5 V. (b) Images of the same surface spot as shown in (a) obtained under ambient conditions. The domain-wall contrast is the weakest at the zero potential.

sured in argon had its minimum for all tested tips and samples at negative bias voltages. A positive charge has been induced in the tip while applying a negative potential to the sample in order to compensate the electrostatic force. We conclude that the nonzero electrostatic force at zero external potential is attributed to a permanent negative charge in the tip.

There are two reasons for the larger shift of the minimum of the electrostatic force in argon compared to the measurements done in air. Under ambient conditions, free charge carriers can compensate the charge on a tip or a sample. Additionally, the water film which is present on all surfaces reduces the Coulomb force because of the high dielectric constant of water ($\epsilon_r=81$).

The difference in the electrostatic tip-sample interaction as observed in argon compared to air should also influence the imaging process of ferroelectric domains with the EFM. The domain structure of GASH has been measured in the dynamic operation mode of the microscope. A molecularly flat surface area has been chosen for the experiments in order to avoid cross talk from the topography on the electrostatic signal. Figure 3(a) shows the domain structure as revealed at different bias voltages in argon atmosphere. Domain walls appear as lines. There is no observed contrast from domains. The occurrence of a domain-wall contrast can be explained by the induction of a dipole in the tip due to the electric field from the domain structure in the sample.⁹ The force gradient acting on the dipole is the strongest in the inhomogeneous field at the domain boundaries. The application of an external voltage changes the magnitude of the domain-wall contrast. The contrast is the strongest at a voltage of 5 V and the weakest at -5 V.

After finishing the measurements in argon [Fig. 3(a)] the microscope and sample have been exposed to ambient conditions, and the same surface spot has been scanned again in

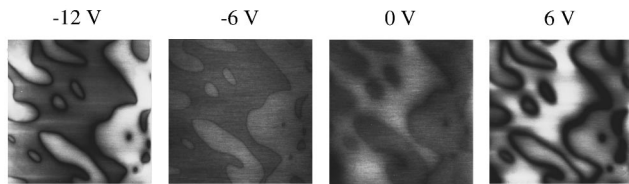


FIG. 4. Electrostatic contrast on GASH (0001) as revealed in argon atmosphere using the static noncontact mode. The surface of the $30 \times 30 \mu\text{m}^2$ area is smooth. The images were taken using a gold-coated silicon nitride cantilever ($k=0.6 \text{ N/m}$) at a tip-to-sample distance of 70 nm. The domain walls are visible in all images as dark lines. Additionally, the domains give a contribution to the electrostatic contrast. The domain contrast can be inverted by a change in the sign of the bias voltage. The bright domains in the image observed at -12 V bias are recognized as positive ones, the dark domains as negative ones (for explanation see text).

the dynamic operation mode using the same cantilever and scan parameters. As observed in experiments in the argon atmosphere, domain walls appear visible, and no contribution from domains to the electrostatic contrast has been observed. However, the change of the domain-wall contrast in dependence on the externally applied voltage differs in comparison to the results obtained in argon atmosphere. Under ambient conditions, the domain contrast is the weakest at values around zero potential.

The EFM investigations carried out in the dynamic operation mode of the microscope are sensitive to the force gradient. However, it is often desirable to measure directly the electrostatic force which arises from the sample stray field. Therefore, the ferroelectric domain contrast has been revealed in the static noncontact operation mode of the microscope. In this mode we have measured forces while scanning the tip over the sample surface at the predetermined height.

Again, a smooth surface area has been chosen for the investigation. Figure 4 shows the results obtained in argon atmosphere. Here, dark contrast means an attractive force on the tip. The domain walls are always visible as narrow dark lines, regardless of the applied bias voltage. Additionally,

neighboring domains exhibit a different electrostatic contrast. The sign as well as the magnitude of the domain contrast depend on the applied bias voltage.

The domain and domain-wall contrast revealed in the static operation mode can be explained considering electrostatic charges within the tip. First, the electrostatic stray field of the sample induces an electric dipole in the tip. Therefore, we have always observed the attractive force exerted on the tip near the domain boundaries. This is in agreement with the observations made in the dynamic operation mode where the domain-wall contrast has been revealed (cf. Fig. 3). Moreover, the applied bias voltage induces an electric charge in the gold layer on the tip. This charge interacts with the surface charges from the domains. By altering the sign of the applied voltage, we change the sign of the induced charge in the tip. Subsequently, the interaction between a tip and surface charge has been changed from attractive to repulsive, or vice versa. Therefore, in the static operation mode the sign of the domain polarity can be determined. As in the experiments in the dynamic mode, the characteristic shift of the minimum of the contrast curve measured in argon environment to negative voltages can be observed.

IV. Summary. It has been shown that the electrostatic force between the tip and the sample differs for measurements done in air compared to those performed in argon atmosphere. A permanent negative charge in the tip causes an electrostatic interaction with the sample even at zero external potential. This electrostatic force is larger in argon, since in air surface charges are partially compensated by free charge carriers coming from the environment. Additionally, the electrostatic force in air is reduced by the contamination layer on the surface which is always present under ambient conditions. The electrostatic force shows a parabolic dependence on an externally applied electric field between a tip and a sample. Domain wall as well as domain contrast has been observed in the dynamic and static noncontact operation mode of the microscope.

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