

Carbon tips as sensitive detectors for nanoscale surface and sub-surface charge

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Abstract

Electrically insulating tips prepared by carbon deposition are used as sensitive detectors of nanoscale charge patterns on cleaved insulating surfaces. Dynamic scanning force microscopy images recorded with a neutral carbon tip reveal the surface topography and strong local charging at step edges while images taken with a charged tip exhibit subtle contrast features resulting from charges located at or beneath the surface of flat terraces. Analysing dynamic phenomena during imaging allows a determination of charge polarity and identifies sub-surface charges as trapping centres for charges exchanged between the tip and the surface. A density of a few hundred charged sub-surface defects per μm^2 is determined on $\text{CaCO}_3(10\bar{1}4)$ while the defect density is one order of magnitude smaller on $\text{CaF}_2(111)$. The method allows the detection of elementary charges at room temperature.

Dynamic scanning force microscopy is an excellent tool for nanoscale and atomic resolution imaging of insulating surfaces and a promising candidate for nano and atomic scale characterization of hybrid nanodevices constructed of electrically conducting and insulating materials [1]. It is a strength of the technique that it is not only capable of measuring surface topography but also a variety of other sample properties, since the force acting between the probing tip and the sample is composed of chemical, electrostatic, van der Waals and possibly further interactions. When dealing with insulating surfaces and nanostructures, the high resolution detection and quantification of charges at the nanoscale is a most important issue. Examples are charges trapped at the surface or sub-surface defects as investigated in the present paper, but also charge accumulation that may be crucial for the function or failure of devices in conventional and molecular nanoelectronics where nanometre-sized insulating structures play an increasingly important role [2]. The standard approach to high resolution charge detection is the Kelvin probe force microscope that is an extension of the dynamic force microscope recording electrostatic forces controlled by

a bias voltage applied between the tip and a conducting sample support [3–5]. This technique is capable of measuring charge patterns in a variety of interesting applications in science and technology, and even atomic scale contrast formation has been demonstrated [6]. However, Kelvin probe force signals are mostly very weak, and their reliable detection requires first, elaborate technical precautions and second, modulating the bias voltage in combination with phase sensitive detection strongly impeding the recording speed.

In the present paper, we introduce an alternative concept of charge detection based on an amplification of charge related tip–surface interaction by using a charged tip in the force microscope. The electrically insulating tip is prepared by electron beam assisted carbon deposition on top of a conventional oxidized silicon tip. The conductivity of such a tip is low enough to facilitate the storage of charge over long times, and charge trapping is strong enough to allow stable imaging over large areas. With these tips, we investigate two different ionic surfaces to demonstrate important features of the technique. Imaging on a cleaved $\text{CaCO}_3(10\bar{1}4)$ surface with a neutral carbon tip reproduces the surface topography

with highest resolution and provides atomic resolution, while a charged carbon tip reveals stable patches of sub-surface charge that can neither be detected by a neutral tip nor by a conventional oxidized silicon tip. In a CaF_2 crystal cleaved along its (111) surface, we identify only very few sub-surface charge centres which in some cases appear to act as traps for mobile surface charges deposited from the tip. More frequently we observe the exchange of charge between the tip and the surface at step edges but also find evidence that sub-surface charges may act as trapping centres for mobile surface charges deposited from the tip. Monitoring the force response to events of picking up and dropping off charges at trapping centres during scanning allows us to determine the charge polarity and facilitates the understanding of the observed contrast patterns.

The experiments were performed with a commercial dynamic force microscope in an ultra-high vacuum system operated at a base pressure in the low 10^{-10} mbar range. We used silicon cantilevers with a resonance frequency between 70 and 80 kHz and tips that were covered with a native oxide layer. The tip shape was examined with a field emission scanning electron microscope that was also used for electron beam assisted carbon deposition, a technique that has been used to fabricate high aspect ratio force microscopy tips [7–9]. We find that this method allows the preparation of tips with a length of typically 50 nm and a tip radius that is often considerably smaller than that of the oxidized silicon tip. Our carbon tips have an apex radius of typically some nanometres and are found to be remarkably robust against crashing them into the surface. Therefore, we conclude that they contain a high fraction of sp^3 binding, explaining their good insulating properties. After transferring the cantilevers from the electron microscope into the measurement chamber, we bake the setup at 110°C for 50 h to clean the tips and chamber walls from weakly bound contaminants. The samples are high quality commercial CaCO_3 and a CaF_2 crystals cleaved *in situ*. As the surfaces of both crystals are chemically rather inert, we can perform measurements on clean surfaces for several days before a fresh surface is prepared by further cleavage. To compensate for surface potential differences and global charging, a bias voltage (V_{bias}) between the tip and the metallic plate supporting the back side of the crystal is applied and adjusted to minimize the overall electrostatic forces. If the overall charging is found to be too strong, it is removed by heating the sample to about 50°C . CaCO_3 crystals are often strongly charged immediately after cleavage, and in this case, a sample potential larger than 10 V is found. The extent of charge removal by heat treatment differs strongly from one cleavage to another. We anticipate that this is related to the content and structure of defects created during growth, handling and cleavage of the crystals. For scanning regions wider than $50 \times 50 \text{ nm}^2$, topographic images are taken in the constant frequency shift mode. When scanning smaller areas, especially for obtaining atomic resolution, images of the detuning signal are recorded in the constant height mode [10].

In a first set of experiments, a $\text{CaCO}_3(10\bar{1}4)$ surface is investigated with a silicon tip and two different carbon tips where measurements with carbon tips I and II are performed in the same areas and immediately after recording images with the silicon tip. Imaging results and scanning electron micrographs of the silicon tip and carbon tip I are shown in

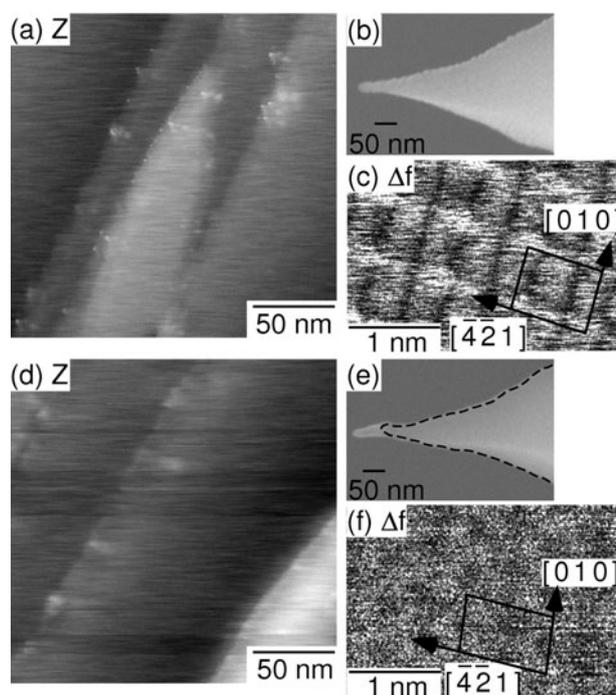


Figure 1. (a) Force microscopy topography image of $\text{CaCO}_3(10\bar{1}4)$ taken with an oxidized silicon tip (parameters: $\Delta f = -5.3 \text{ Hz}$, $f_0 = 76.932 \text{ Hz}$, $V_{\text{bias}} = +3.3 \text{ V}$). (b) Scanning electron micrograph of the silicon tip used in this experiment. (c) The same surface imaged in constant height mode with the silicon tip yielding atomic resolution (mean $\Delta f = -20 \text{ Hz}$). (d) Topography image taken at the same surface with carbon tip I (parameters: $\Delta f = -3.4 \text{ Hz}$, $f_0 = 76.333 \text{ Hz}$, $V_{\text{bias}} = +1.3 \text{ V}$). (e) Scanning electron micrograph of carbon tip I. Carbon was deposited in the electron microscope with the electron beam focused onto the silicon tip (contour shown as the dashed curve). (f) The same surface imaged in constant height mode with the carbon tip yielding atomic resolution (mean $\Delta f = -62 \text{ Hz}$).

frames (a)–(c) and (d)–(f) of figure 1, respectively. Figure 1(a) shows a topography image of the $\text{CaCO}_3(10\bar{1}4)$ surface taken with a silicon tip that is shown in frame (b). The topography is dominated by atomically flat terraces of typically some ten nanometres width and steps with a height of 0.3 nm corresponding to the distance of neighbouring $(10\bar{1}4)$ planes. Bright spots along the steps correspond to charge patches as we frequently observe them at step edges of cleaved insulating crystals. A zoom-in image taken in the constant height mode at the centre of frame (a) is shown in frame (c), and demonstrates the atomic level structural integrity and cleanliness of the surface. The protrusions apparent in this image represent the CO_3^{2-} group, and the observed pattern allows an identification of crystal orientations. For a detailed discussion of atomic scale contrast formation on $\text{CaCO}_3(10\bar{1}4)$, however, we refer to a forthcoming paper. The images shown in figures 1(d) and (f) were obtained with carbon tip I that is shown in some detail in frame (e). This tip was prepared by electron beam assisted carbon deposition onto the apex of the silicon tip shown in frame (b). The results demonstrate that contrast formation in the van der Waals regime is almost the same as for the silicon tip (large scale image shown in frame (d)) while the atomic scale contrast shown in frame (f) is much weaker for the carbon tip than for the silicon tip. This is an expected result as the interaction strength of a covalently bound cluster with

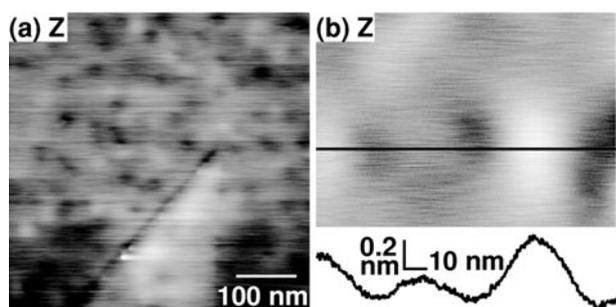


Figure 2. (a) Force microscopy topography image of $\text{CaCO}_3(10\bar{1}4)$ taken with carbon tip II (parameters: $\Delta f = -1.2$ Hz, $f_0 = 77.490$ Hz, $V_{\text{bias}} = +3.9$ V). (b) Topography image of a magnified area taken on the large terrace of frame (a). The curve at the bottom shows a profile of the apparent topography taken along the line drawn in the image.

the ionic surface is comparable with that of the polar cluster formed by the oxide (or contamination) of the silicon tip only if a dangling bond is present [11]. This is not the case for the carbon tip where the bonds are well saturated. While details of atomic scale imaging with carbon tips will be investigated in detail in a forthcoming publication, here we note that carbon tip I yields contrast patterns that are qualitatively not different from those obtained with the silicon tip.

As illustrated in figure 2, the situation dramatically changes when imaging with a second carbon tip, referred to as carbon tip II. Frame (a) represents a topography image obtained with carbon tip II immediately after having checked by imaging the surface with an oxidized silicon tip (image not shown) that the surface is clean and structurally perfect as in the former experiments. The image recorded with carbon tip II exhibits strong nanoscale roughness. Image analysis as shown in the magnified image of frame (b) reveals that the apparent corrugation is due to nanometre-sized depressions and protrusions modulating the topography by a few hundred picometres. As the investigation of terraces with both the silicon tip and carbon tip I clearly reveal a perfectly smooth and stoichiometric surface evidenced down to the atomic scale, the apparent roughness cannot be due to topographic or chemical surface irregularities. Instead, we interpret the corrugation to be a result of charge patches located beneath the surface where nanoscale contrast formation is due to long range electrostatic interactions between the charge patches and the tip. We also note that it is not possible to obtain atomic resolution images with carbon tip II, although nanoscopic structures are well reproduced with this tip. This observation is in accordance with the general finding that strong local charging prevents atomic resolution imaging as fluctuations due to long range electrostatic interactions obscure subtle atomic contrast features.

The results shown in figures 1 and 2 demonstrate that electrostatic interactions take place between charges in the crystal and charges permanently located at the carbon tip end. Within this interpretation, carbon tip I is electrically neutral while carbon tip II is charged. In a series of experiments with several different carbon tips, we find consistently that on the very same $\text{CaCO}_3(10\bar{1}4)$ surface, a tip either yields flat terraces as found for carbon tip I or apparent nanoscale corrugation as found for carbon tip II and, therefore, we separate the tips into

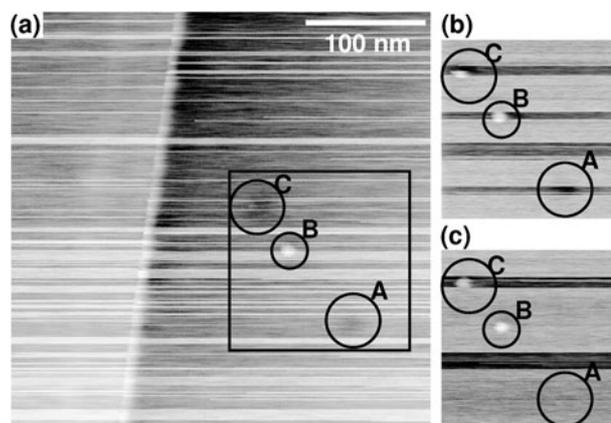


Figure 3. Force microscopy topography images recorded consecutively on $\text{CaF}_2(111)$ with carbon tip II ($\Delta f = -1.4$ Hz, $f_0 = 77.488$ Hz, $V_{\text{bias}} = +2.0$ V). Frames (b) and (c) correspond to the square region marked in frame (a) and show the development of the apparent contrast of defects A, B and C and its response to changes in the tip charge state. The horizontal stripes result from changes in the charge state of the tip and the surface that often occur at the step edge or at sub-surface defects appearing as shallow depressions, while the bright apparent protrusions represent surface charges.

two classes, neutral and charged tips, respectively. Scanning results are found to be reproducible and stable for imaging with tips from one of the classes and we find that the charge state of a tip does not change during scanning on $\text{CaCO}_3(10\bar{1}4)$.

To investigate the tip charges and related phenomena of contrast formation in more detail, we extend experiments to a cleaved $\text{CaF}_2(111)$ surface where we had observed a localization of charges at step edges and frequent charge exchange between tip and surface in previous experiments. We again checked by nanoscale and atomic resolution imaging with an oxidized silicon tip that the terraces are atomically flat and clean. Scanning results obtained with carbon tip II are displayed in figure 3, where we find a step separating left and right terraces in the survey frame (a). The dominant feature in this frame as well as consecutively recorded frames are multiple stripes aligned parallel to the fast scanning direction. We find that stripes frequently start or terminate at the step edge, and attribute this to charge exchange between the tip and the surface initiated by the strong interaction present at the step edge. We exclude particle exchange as a possible origin of the stripes as we could show in previous studies that tip instability involving particle exchange is always associated with a strong change in contrast in the dissipation signal recorded during scanning [10], while we did not observe any measurable dissipation contrast in the present scans. These measurements indicate that contrary to the findings for $\text{CaCO}_3(10\bar{1}4)$, there are mobile charges on the $\text{CaF}_2(111)$ surface that can frequently be exchanged between the tip and the surface and are presumably trapped as weakly bound charges by special centres located at the tip apex.

Besides the stripe patterns, we find very few irregularities exhibiting contrast features similar to those due to charged sub-surface defects found for imaging on $\text{CaCO}_3(10\bar{1}4)$. A closer inspection reveals three kinds of defects in the form of bright and dark dots. Defect A appears as an apparent depression less than 0.1 nm deep, defect B as a protrusion of about 0.6 nm

height, and defect C as a protrusion of about 0.1 nm height with a depression and a larger dark region surrounding the protrusion. Frames (b) and (c) show the development of defect related contrast features in consecutively recorded images. The defects do not only have different signatures but their apparent contrast features respond differently to changes in the tip charge state. In frame (b), defect A appears as a depression of about 0.2 nm depth in a dark stripe, while the defect contrast disappears in the adjacent brighter regions. The defect is completely invisible in frame (c), where the respective region appears as a homogeneously grey shaded area. We anticipate that defects appearing as a depression are stable sub-surface charge defects, while the changes in their apparent contrast are due to a variation of tip–surface distance upon a change in the tip charge state. This explains why defect A is clearly visible within a dark stripe where the tip is close to the surface (frame (b)) and disappears when the tip is retracted (frame (c)). As defect B appears as a stable protrusion in a large number of consecutively recorded images, we speculate that this is a stable charged defect at the surface rather than a sub-surface defect, but we cannot exclude that it is a topographic feature. The latter explanation is, however, rather improbable since we have not observed such surface defects during years of investigating the $\text{CaF}_2(111)$ surface with silicon tips.

The most interesting dynamic effects are observed for the charge defect C that initially appears as a protrusion of about 0.4 nm height in figure 3(b). Following the slow scanning direction from the bottom to the top of the frame, the contrast undergoes several significant changes. Most obvious is that the apparent protrusion suddenly disappears and the feature left is a larger apparent depression of 0.2 nm depth surrounding the position of the former protrusion. In frame (c), defect C reappears as a protrusion, indicating that this bright feature is due to a charge exchanged between the tip and the surface that may be trapped by the sub-surface defect. A detailed analysis of traces recorded in the vicinity of defect C illustrated in figure 4 allows a consistent interpretation of charge exchange events, and the polarity of the exchanged charges can be inferred from the polarity of the bias voltage applied between the tip and the back side support of the sample. A sample bias of +2.0 V was applied to minimize the interaction of the positively charged tip with a negatively charged surface (see the schematic drawing in figure 4) before recording the images shown in figure 3. This bias voltage compensates the charge related forces in the dark stripes seen in frames (a)–(c). According to the scheme shown in figure 4, this corresponds to a compensation for a tip having a small positive charge. Charge exchange events result in temporarily larger tip charging. The left-hand side image in figure 4 is a magnified view of defect C as it appears in figure 3(b), while individual traces (a)–(g) along the fast scanning direction extracted from this image are compiled and interpreted on the right-hand side. The sub-surface defect is an accumulation of positive charge that is imaged as a depression as the repulsive interaction with the positive tip end is compensated by a tip approach by the feedback loop. This defect may trap and release a negative surface charge that appears as a protrusion. In traces (c) and (g), we observe the pick up and drop off of a negative charge by the tip in the vicinity of the positive sub-surface defect associated with a decrease and increase in signal level, respectively. The

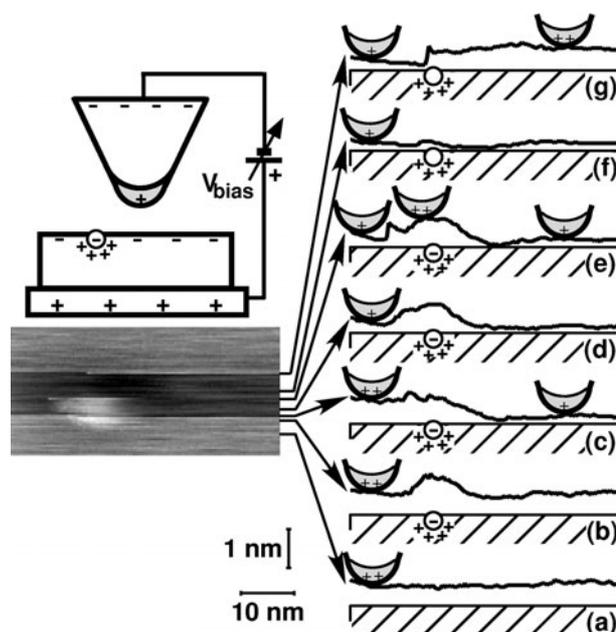


Figure 4. Schematic drawing of the tip–surface configuration illustrating the distribution of the charges and the polarity of the bias voltage V_{bias} present in the experiment on $\text{CaF}_2(111)$. The image below is a magnified view of the area around defect C as it appears in figure 3(c). The alterations in apparent contrast during scanning in this area are interpreted in the text by analysing scan lines (a) to (g) taken at various positions across the sub-surface defect that appears as a dark contrast feature. The schematics shown in the scan lines illustrate the charge state of the tip and the surface defect.

spike appearing in trace (e) indicates a change in the tip charge state for a very short time during the interaction with the sub-surface defect. The negative surface charge is completely removed during the time elapsed between recording trace (e) and trace (g), possibly by the charge exchange event observed in trace (e). Note, however, that changes in the charge state of the tip are not necessarily correlated with changes of surface charge, indicating that the charges are rather mobile at the surface.

In summary, the described experiments provide insight into the processes of charge trapping and charge transfer at insulator surfaces, and we have introduced a technology for a simple, fast and sensitive characterization of nanoscale charges in insulating systems. We find two types of charges and charging behaviour of surfaces. First, stable charges firmly attached to the tip via deep trapping centres that define the nature of the tip being a *charged tip* or a *neutral tip*. Second, mobile charges that may readily be attached to or released from shallow trapping centres of the tip and demonstrate surface mobility. While imaging on $\text{CaCO}_3(10\bar{1}4)$ reveals a large number of stable patches of trapped charges on terraces, the charges appear to be highly mobile on $\text{CaF}_2(111)$ and are mainly trapped and released at step edges while only very few trapping centres are observed on terraces. Such measurements directly visualize charged sub-surface defect structures that are most difficult to identify with other methods. Analysing images like the one shown in figure 2(a) yields a defect density of a few hundred per μm^2 on $\text{CaCO}_3(10\bar{1}4)$. While further studies may unravel the detailed origin of charge trapping centres, here we speculate that the trapping centres are

dislocations or impurities created during the growth, handling and cleavage of the sample.

Neglecting fluctuations due to mobile charges, the tips are found to be either charged or neutral, depending on the amount of charge present in the deep trapping centres, but presently there is no straightforward way of deliberately manipulating the character of the tip. However, nanotechnology might provide a simple tool for permanently charging a force microscopy tip. It is known that carbon nanotubes are well suited as highly effective field emitters delivering highly focused electron beams [12]. Such a field emitter could be integrated into a charge sensing force microscope to produce a charged tip by controlled electron bombardment creating defects for anchoring charges.

The ultimate goal of the charge sensing tool introduced here is the detection of single electrons trapped in nanoscopic structures. Such sensitivity can presently be reached only by utilizing ultra-sensitive force detection operated at low temperature [13]. In the following, we determine the sensitivity limit of the charged tip detection scheme. Applying a standard approach for calculating tip-sample interaction [14], we roughly estimate the tip-sample distance to be in the range of 1–2 nm. The precision of this result is limited, as we do not precisely know the composition of the tip and, hence, the effective Hamaker constant⁴. Based on this result, we determine the Coulomb interaction energy of two elementary charges placed 0.3 nm beneath the surfaces of tip and sample, respectively, assuming a tip-sample distance of 1.5 nm. Including screening effects, the calculation yields an apparent change in tip-surface distance of 0.3 nm when removing an elementary charge from the tip, which is well in accordance with the experimental observation. We further find an interaction energy of 2×10^{-20} J for a singly charged tip with the surface charge, which is about one order of magnitude larger than the thermal energy of 4×10^{-21} J at room temperature. Hence, the calculation clearly demonstrates that

our technique allows the detection of elementary charges even at room temperature.

The time resolution for monitoring charge transfer events in our experiments is solely limited by the scanning speed and pixel density of image acquisition and not by the response time of the detection system, and there is plenty of room for further instrumental improvement. Placing the tip above a charged nanostructure and monitoring the force response with an ultra-sensitive detection scheme will in future allow a real-time measurement of charge transfer in functional nanodevices at the single electron level.

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⁴ We assumed a Hamaker constant of 7×10^{-20} J representing a CaF₂ nanotip (often created by pickup of material from the surface) interacting with a CaF₂ crystal.