Quantitative phase-mode electrostatic force microscopy on silicon oxide nanostructures

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Summary
Phase-mode electrostatic force microscopy (EFM-Phase) is a viable technique to image surface electrostatic potential of silicon oxide stripes fabricated by oxidation scanning probe lithography, exhibiting an inhomogeneous distribution of localized charges trapped within the stripes during the electrochemical reaction. We show here that these nanopatterns are useful benchmark samples for assessing the spatial/voltage resolution of EFM-phase. To quantitatively extract the relevant observables, we developed and applied an analytical model of the electrostatic interactions in which the tip and the surface are modelled in a prolate spheroidal coordinates system, fitting accurately experimental data. A lateral resolution of ~60 nm, which is comparable to the lateral resolution of EFM experiments reported in the literature, and a charge resolution of ~20 electrons are achieved. This electrostatic analysis evidences the presence of a bimodal population of trapped charges in the nanopatterned stripes.

Introduction
Open-loop electrostatic scanning probe microscopy techniques enable the mapping of the electrostatic interaction between a conductive atomic force microscopy tip, held to bias voltage $V$ (DC or AC), and the sample surface. For instance, the charge distribution in finite size systems (Yalcin et al., 2012; Roy-Gobell et al., 2015; Miyahara et al., 2017), even in the presence of spatial, compositional and energy disorder (El Khoury, 2017), can be visualized by these techniques. Local electrostatic techniques provide information on the 2D spatial distribution of charge carriers in semiconductors (Chin et al., 2008; Musumeci et al., 2017), nanostructures (Krauss & Brus, 1999; Cherniauskaya et al., 2003; Marchi et al., 2008; Borgani et al., 2016) and devices (Pingree et al., 2009) and, more recently, in volume (3D) (Collins et al., 2015; Fabregas & Gomila, 2020) and in time (Araki et al., 2019; Borgani & Haviland, 2019; Mascaro et al., 2019). These techniques were proven useful in studying the localization of trapped charges in thin films (Silveira & Marohn, 2004; Chen et al., 2005a; Chen et al., 2005b; Muller & Marohn, 2005), quantum dots (Tevaarwerk et al., 2005) and nanotubes (Chin et al., 2008); to measure the resistance at metal–semiconductor interfaces and grain boundaries in operating devices (Annibale et al., 2007); to relate electrical properties, such as dielectric permittivity (Gramse et al., 2009; El Khoury et al., 2016; Fumagalli et al., 2018), conductivity (Castellano-Hernández & Sacha, 2015; Aurino et al., 2016), piezoelectricity (Moon et al., 2017) and percolation pathways (Barnes & Buratto, 2018), directly to the organization of the material at the mesoscopic length scales. Charge distribution in supramolecular architectures (Dabirian et al., 2009; Borgani et al., 2014; Garrett et al., 2018), biomolecules (Gil et al., 2002; Cuervo et al., 2014; Dols-Perez et al., 2015; Lozano et al., 2018; Lozano et al., 2019), living organism (Esteban-Ferrer et al., 2014; Van Der Hofstad et al., 2016a; Van Der Hofstad et al., 2016b) and 2D materials (Collins et al.,...
Electrostatic interactions are monitored by the change on either the amplitude \( A \) (Martin et al., 1988) or the phase \( \phi \) (García & Pérez, 2002; Kim et al., 2011) of the oscillating cantilever, depending on the operation mode (Weaver & Abraham, 1991; Annibale et al., 2007). Our work here focuses on phase-mode electrostatic force microscopy (EFM-Phase), which is a potentiometric technique where the contribution of electrostatic interactions is quantified according to their effect in the oscillation phase of the cantilever. For this reason, the term EFM-Phase has become widely adopted (Lei et al., 2004). In order to single out the topographical contributions dominated by shorter range van der Waals interactions, EFM-Phase is often operated in dual pass technique (Martin et al., 1988) where a topographic scan-line is followed by an interleave scan-line. In the first pass, the surface topography is recorded in the amplitude modulation AFM imaging method: in the second pass, the tip is retracted at a fixed height \( z = H \) above the surface and scanned along the previously recorded topographic profile by applying a bias voltage with respect to the grounded substrate. Thus, the phase signal detected with the cantilever minimizes topography effects, as it depends exclusively upon the electrostatic interaction between the oscillating tip and the surface held at a constant separation.

When the tip is far from the sample \( (z \gg H) \), the phase \( \phi \) of the free cantilever oscillations is \( \pi/2 \), delayed with respect to the sinusoidal signal that drives the cantilever oscillation. When the tip interacts electrostatically with the surface \( (z = H) \), a phase lag \( \Delta \phi \) (in radians) occurs in the cantilever oscillations (Lei et al., 2004). Following Cleveland et al. (1998), the phase in interaction \( \phi_i \) will be \( \pi/2 + \Delta \phi \) with \( \phi_i > \pi/2 \) or \( \phi_i < \pi/2 \) for attractive and repulsive coulombic forces, respectively.

The phase lag \( \Delta \phi \) depends linearly on the normal component of the force gradient, i.e. \( F_z \) (in N) (Kim et al., 2011):

\[
\Delta \phi = -\frac{Q}{k} \frac{dF_z}{dz}, \tag{1}
\]

where \( Q \) is the cantilever quality factor (dimensionless) and \( k \) is the unperturbed spring constant of the cantilever (in N m\(^{-1}\)).

The EFM-Phase tip–sample system can be approximated by a mutual capacitance \( C \) consisting of two conductive surfaces separated from each other by a dielectric material (i.e. air, vacuum or liquid electrolyte). Upon the assumption of rotational symmetry of the tip, the change of the tip–sample capacitance \( C(x, y, z) \) is mostly due to the tip–sample distance, thus \( C(x, y, z) \approx C(z) \). When a biased tip is brought close to an electrically neutral substrate (grounded), it causes a separation of charge within the sample. The effect of the closer (opposite polarity) charges causes an attractive force \( F_z \) that increases for decreasing tip–sample distance \( z \). The effect is most pronounced when the sample is an electrical conductor as the charges are free to move across the sample. The energy stored in the tip–sample capacitor \( U_c \) is, therefore, equal to the work required to accumulate sample charges below the tip, which is proportional to the force exerted by tip surface charges along the \( z \) direction (force direction from tip to sample):

\[
U_c = \frac{1}{2} CV^2, \Rightarrow F_z = -\frac{dU_c}{dz} = -\frac{V^2}{2} \frac{dC}{dz} \Rightarrow \Delta \phi = \phi_i - \pi/2 = -\frac{Q}{k} \frac{dF_z}{dz} = \frac{Q \cdot V^2}{2 \cdot k} \frac{dC}{dz}, \tag{2}
\]

where \( V \) is the voltage difference between the tip and the sample. The curvature of the capacitance \( d^2C/dz^2 \) at the tip position \( (x, y, z) \) is extracted by measuring the phase \( \phi_i \) while scanning the surface with different voltages applied to the tip \( (V_{tip}) \). As shown in Eq. (2), the function \( \phi(V) \) is a concave upward parabola with axis of symmetry \( V = 0 \) and vertex \( (0, \pi/2) \). The capacitance \( C \), and consequently its second derivative \( d^2C/dz^2 \), is fixed for a given geometry, therefore, the arms of the parabola, for similar geometrical configurations, are stretched by the ratio \( Q/k \). In the event that static charges are present on either sample or tip surfaces due to doping (Gupta et al., 2007; Qi et al., 2008) or a dipole layer due to adsorbed chemical species (Mugo & Yuan, 2012), the parabola will be translated of a bias offset \( V_0 \), and \( V \) will be equal to \( (V_{tip} - V_0) \). Accordingly, a quantitative use of EFM-Phase data requires an accurate and stable measurement of the parabola \( \phi(V) \), together with a realistic tip geometry for extracting the local electrical properties from the capacitance.

Here, an experimental protocol suitable to perform reproducible electrostatic measurements by means of EFM-Phase is demonstrated and an interpretative framework to carry out a quantitative analysis of EFM-Phase images is proposed. A description of the tip–sample interactions in probe spheroidal coordinates is adopted, which allow us to implement a three-dimensional (3D) geometry of the tip. This framework was also used by Keller to describe tip–surface convolution effects in scanning probe microscopies (Keller, 1991). Within this framework, an effective radius of electrostatic interaction can be extracted and used as a figure of merit to quantify the electrostatic lateral resolution of EFM-Phase. The method is assessed by evaluating the electrostatic charge in silicon oxide nanostructures fabricated by oxidation with scanning probe lithography (o-SPL) of native silicon oxide (Garcia et al., 2006). This charge is trapped in the growing oxide during the electrochemical reaction as it was shown earlier by scanning capacitance microscopy (Dagata et al., 1998) and Kelvin probe force microscopy (Chiesa & Garcia, 2010). EFM-Phase shows
that the charge in the nanofabricated silicon oxide stripes (from here stripes) is distributed nonhomogeneously within a stripe and from one stripe to another. Some stripes do not exhibit trapped charges, although they were fabricated in the same batch. Thus, the pattern fabricated by o-SPL appears a convenient testbed sample for assessing the resolution of EFM-Phase.

The paper is organized as follows: Section ‘EFM-Phase measurements’ presents the details of EFM-Phase operation as well as its theoretical description; Section ‘Spatial resolution in EFM-Phase’ describes our proposed analytical model describing the capacitance of the tip–sample system using prolate spheroidal coordinates and discusses its lateral resolution; Section ‘EFM-Phase on SiO₂ stripes: inhomogeneous charge distribution’ presents and discusses the experimental results on the silicon oxide stripes. Finally, Section ‘Conclusions’ summarizes the major results.

**EFM-Phase measurements**

EFM detects the electrostatic interactions between the sample surface and an oscillating conductive AFM probe biased with a DC voltage. Both conservative forces and dissipative forces contribute to the phase shift in EFM measurements although the conservative forces, i.e., the electrostatic forces, are dominant with respect to the dissipative one, especially for Q ≫ 1 (typical EFM cantilevers have Q > 250) (Sader & Jarvis, 2006).

In the absence of an interaction, the cantilever is forced to oscillate at its resonant frequency ω₀ with amplitude A₀ by a piezoelectric actuator driven with a sinusoidal wave with amplitude Aexc (100 or 200 mV) and frequency ω₀ (from ≈150 to ≈300 kHz).

In the second pass of EFM-Phase measurements, the tip is retracted at fixed distance H > 20 nm, a bias voltage is applied to the tip and the AFM feedback loop is switched off. Although the tip scans the surface, the force gradient can be measured along the z direction due to electrostatic interactions at each point (x, y, z). For small vibrational amplitudes and small force gradients, the force acting on the tip can be expanded at the first order as Fz(z) = Fz(H) + (dFz/dz) · δz. For convenience, an attractive force pointing toward the sample is negative and its derivative is positive, therefore, for attractive forces −Fz(z) = −Fz(H) + (dFz/dz) · δz. By deriving such equation in δz, one obtains −δFz(z)/δz = δFz(H)/δz + (dFz/dz) or, equivalently, −keff = −k + (dFz/dz). The derivative of an attractive force along the normal to the surface, dFz/dz, reduces the spring constant k to an effective spring constant keff = k − dFz/dz. On the other hand, the resonance frequency ω₀ (ω₀ = k/√m) shifts to ωeff given by ωeff = ω₀/√(k_0/m) = ω₀/√[(k − dFz/dz)/m] = ω₀/√[(k/m) · (1 − dFz/dz/k) = ω₀ · √(1 − dFz/dz/k). Being (dFz/dz/k) · k⁻¹ ≪ 1, the square root is expanded in Taylor series giving ωeff ≈ ω₀ · (1 − dFz/dz/2k).

The effective resonant frequency ωeff decreases in value continually as the tip approaches the surface due to the monotonic increase in the force gradient (Martin et al., 1987).

The phase angle ϕf(ω) (in radians) of a free cantilever oscillation is expressed as (Whangbo et al., 1998):

\[ ϕ_f(ω) = \tan^{-1}\left( \frac{mω_0ω}{Q(k − mω^2)} \right) \tag{3} \]

The phase curve is centred at the resonance frequency ω₀, where ϕf(ω₀) = π/2. According to the harmonic approximation of ref. (Whangbo et al., 1998), the phase curve of an interacting cantilever ϕi(ω) is obtained from Eq. (3) by substituting k → keff and ω₀ → ωeff:

\[ ϕ_i(ω) = \tan^{-1}\left( \frac{mω_0ω_{eff}}{Q(k_{eff} − mω^2)} \right) \]

\[ = \tan^{-1}\left( \frac{ω_0ω_{eff}}{Q(k_{eff} − mω^2)} \right) \tag{4} \]

Figure 1 shows the experimental amplitude spectrum of the cantilever (normalized) and its corresponding phase acquired out of the tip–sample interactions. At the onset of the tip–sample electrostatic interaction, the tip is automatically retracted and fixed at a height H, then a constant bias is applied...
to the tip and the AFM feedback loop is switched off. Along the second pass, the amplitude spectrum is not affected for small force gradients (Whangbo et al., 1998), i.e. \((dF_x/dz)k^{-1} \ll 1\), so the oscillation amplitude \(A\) remains close to the free oscillation amplitude \(A_0\) (e.g. \(A/A_0 \approx 0.96\) within the shaded area of Fig. 1). Accordingly, the frequency shift \(\Delta \omega\) is very small with respect to the resonance frequency \(\omega_0\), i.e. \(\Delta \omega/\omega_0 \ll 1\) (the half of the dashed area in Fig. 1 is \(\Delta \omega/2 \approx 100\) Hz with respect to a resonance frequency of \(\approx 274\) kHz). In contrast, the phase signal (in radians) is steeped around the resonance frequency \(\omega_0\), ranging from to \(2/5\pi\) to \(3/5\pi\) (see the horizontal shaded area of Fig. 1).

For the experimental conditions described above, \(\omega \approx \omega_0\) and \((dF_x/dz)k^{-1} \ll 1\). Eq. (4) can be rewritten as:

\[
\varphi_i(\omega) \approx \varphi_i(\omega_0) = \tan^{-1}\left( \frac{\omega_0 Q}{k} \frac{1 - \frac{1}{2} \frac{dF_x}{dz}}{ \frac{d^2C}{dz^2} - \varphi_i^2(\omega_0) } \right) = \tan^{-1}\left( \frac{\omega_0 Q}{k} \frac{1 - \frac{1}{2} \frac{dF_x}{dz}}{ \frac{d^2C}{dz^2} - \varphi_i^2(\omega_0) } \right) 
\]

By using the trigonometrical relationship \(\tan^{-1}(x) + \tan^{-1}(x^{-1}) = \pi/2\) and expanding \(\tan^{-1}(x)\) in a Taylor series for \((dF_x/dz)Qk^{-1} \ll 1\), Eq. (5) becomes:

\[
\varphi_i(\omega) \approx \frac{\pi}{2} - \tan^{-1}\left( \left( - \frac{Q dF_x}{k} \right) \frac{1}{2} \frac{dF_x}{dz} \right) \approx \frac{\pi}{2} + \frac{Q dF_x}{k} \frac{d^2C}{dz^2}
\]

that fully satisfy the Cleveland notation (Cleveland et al., 1998), i.e. the phase in interaction \(\varphi_i(\omega)\) is \(\pi/2\).

On each scanned point (image pixel) with coordinates \((x, y, z)\), the phase shifts above or below \(\pi/2\) for attractive or repulsive force gradients, respectively. As described elsewhere (Sulchek et al., 2002), the phase \(\varphi_i(\omega)\) takes a transient time to reach a new phase value of about 120 \(\mu\)s. Scan rates of 0.8 Hz (or slower) avoid transient effects because of 256 pixels per line corresponds to a residency time of 4.9 ms per pixel.

Equation (2) implies that it is not sufficient to operate EFM at constant bias (Sun et al., 2007). Instead it is necessary to acquire a set of phase \(\varphi_i(\omega)\) versus \(V\) curves to quantify the local curvature of \(C(\omega)\) by fitting the parabola of Eq. (2) (Gupta et al., 2007).

To investigate the bias voltage dependence of the phase, EFM-Phase experiments are performed on a 200 nm thick Au polycrystalline film, deposited at RT on glass primed with a 5 nm Cr layer (AFM, Solver Smena, NT-MDT, Zelenograd, Moscow, RU). EFM-Phase images were performed with cantilevers with different metal coatings (Table 1). The range of the tip voltage \(V_{tip}\) and the height of the second pass \(H\) are varied in order to keep \(\varphi_i(\omega)\) in the maximum sensitivity range (dashed area of Fig. 1). The measured phase value for each \(V_{tip}\) and \(H\) is the mean value (±the standard deviation) obtained by fitting the phase values distribution measured on a 3 \(\mu\)m \(\times\) 3 \(\mu\)m EFM-Phase image with a Gaussians distribution (see Supporting Information).

The experimental data of Figure 2 show the dependence of the phase \(\varphi_i(\omega)\) (in radians) with respect to the bias voltage applied to the tip \(V_{tip}\). The data are fitted with the parabola:

\[
\varphi_i(\omega) = \left( \frac{\pi}{2} - a \right) + b \cdot (V_{tip} - c)^2
\]

where the parameter \(a\) (dimensionless) considers the deviation from \(\pi/2\) due to noise, mechanical coupling of the cantilever, error in the phase centring procedure; the parameter \(b\) (in \(V^{-2}\)) is the parabola stretching, and represents the sensitivity of the phase measurement; parameter \(c\) (in \(V\)) is the horizontal translation \(V_{tip}\) of zero voltage (\(V_{tip} = 0\)) due to the contribution of the static charges, polarization and the work function difference between tip and surface. Several types of silicon cantilevers with different conductive coatings were employed for the EFM-Phase measurements: NT-MDT NSG10/Pt (resonant frequency \(\omega_0\) of \(\sim 255\) kHz, elastic constant \(k\) ranging from \(3.1\) to \(\sim 37.6\) \(\text{N m}^{-1}\), NT-MDT NSG10/Au (\(\omega_0\) \(\sim 254\) kHz, \(k\) from \(3.1\) to \(\sim 37.6\) \(\text{N m}^{-1}\), NT-MDT NSG01/CoCr (\(\omega_0\) \(\sim 193\) kHz, \(k\) from \(\sim 1.5\) to \(\sim 15.1\) \(\text{N m}^{-1}\)) and Nanosensors CDT-NCHR (\(\omega_0\) \(\sim 361\) kHz, \(k\) from \(\sim 23\) to \(\sim 225\) \(\text{N m}^{-1}\)).

Table 1. Summary of cantilever specifications and fitting data of EFM-Phase on polycrystalline Au.

| \(k\) \(\text{(N m}^{-1}\)) | \(Q\) \(\text{(m N}^{-1}\)) | \(H\) \(\text{(nm)}\) | \(d^2C/\text{dz}^2\) \(\times10^{-1}\) \(\text{FM}^{-2}\) | \(V_0\) \(\text{(V)}\) | \(\Phi_{tip,bulk}\) \(\text{(eV)}\) | \(V_D\) \(\text{(eV)}\) |
|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Au | 7.9 | 255 | 32.3 | 60 | 8.9 ± 0.2 | \(-0.11 ± 0.03\) | 5.1 | \(0.11 ± 0.03\) |
| cd | 20.6 | 302 | 14.7 | 60 | 12.6 ± 0.2 | \(-0.01 ± 0.02\) | [3.5, 5.5] | \([-0.39, 1.61]\) |
| Pt | 9.7 | 256 | 26.4 | 50 | 6.4 ± 0.1 | \(-0.08 ± 0.02\) | 5.65 | \(-0.47 ± 0.02\) |
| Co | 7.5 | 278 | 37.1 | 40 | 2.92 ± 0.03 | \(-0.50 ± 0.01\) | [6.0, 6.5] | \([-0.4, 1.0]\) |

Note: Cantilever elastic constants are calculated by using the Sader method (Sader et al., 1999).
Fig. 2. Phase $\psi_1(\omega)$ vs the applied voltage tip $V_{tip}$ on a 200 nm thick Au polycrystalline film. Several types of silicon cantilevers with different conductive coatings were employed for EFM-Phase measurements. All tips show parabolic trend of $\psi_1(\omega)$ vs $V_{tip}$, an increasingly stretching from Co to Au tips and increasingly negative horizontal translation from cd ($\approx 0$ V) to Co ($\approx 0.5$ V).

Each tip, the results of the fitting are summarized in Table 1, whereas the correspondent parabolas are shown in Figure 2.

The vertical translation $a$ is corrected for each parabola for fixing minima at $\pi/2$.

The term $b = (Q/2k) d^2C/dz^2$, which contains information about the capacitance of the tip–sample system, has the same order of magnitude for different tips, being the parabolas congruent. Starting from Co, which is the relatively lower stretched parabola ($b = (5.42 \pm 0.05) \times 10^{-3}$ V$^{-2}$), the stretching of the parabolas progressively increases up to the Au with $b = (14.4 \pm 0.3) \times 10^{-3}$ V$^{-2}$. Au and conductive diamond (cd) have the same $H$, but the Au parabola is more stretched in reason of its larger $Q/k$ ratio (Table 1). The capacitance curvature $d^2C/dz^2$ decreases progressively from cd ($\approx 13 \cdot 10^{-4}$ Fm$^{-2}$) to Co ($\approx 3 \cdot 10^{-4}$ Fm$^{-2}$), although an increase might be expected due to the decrease in $H$ from 60 to 40 nm. This trend can be explained, in a first approximation, by the increase of the $Q/k$ ratio from $\sim 15$ to $\sim 37$ mN$^{-1}$, in line with the decreasing of $b$ from $\sim 9 \cdot 10^{-3}$ to $\sim 5 \cdot 10^{-3}$ V$^{-2}$. Intriguingly, Au is more sensitive with respect to Co although they have comparable $Q/k$ ratio and Co measurements were performed closer to the surface ($H = 40$ nm). This counterintuitive result can be explained by the reduction of the effective radius of interaction $\rho$ (defined as the radius of the circular projection on the surface plane of the tip portion involved in the electrostatic interaction, i.e., the spatial resolution of EFM-Phase images) when the surface is approached (Colcherco et al., 2001); $\rho$ is reduced from 60 to 20 nm when $z$ passes from 80 to 20 nm, respectively. When the tip is close to the surface ($z \rightarrow 20$ nm) and the lateral resolution is high, only the apical portion of the tip is involved in the electrostatic interaction, therefore, $C(z)$ and its second derivative are small due to the small value of $\rho$. On the other hand, the tip cone is progressively involved in the electrostatic interaction for increasing $z$ and decreasing $C(z)$ values, since larger $z$ values are compensated by increasing $\rho$ (cp. to Section ‘Spatial resolution in EFM-Phase’).

All EFM-Phase measurements show a horizontal translation of the parabolas on the left of $c = 0$, i.e., $c$ values are negative. As reported above, such horizontal translation termed $V_0$ is due to the contribution of the static charges ($Q_{SC}$) and the difference between tip and sample work functions $\Delta \Phi = (\Phi_{tip} - \Phi_{sample})$. As defined in ref. (Novikov & Timoshenkov, 2003), the general form of the tip (or sample) work function $\Phi$, which is valid for metals, insulators and semiconductors, is:

$$\Phi = P + \delta + \chi + V_D,$$

where $P$ is the energy band curvature on the surface; $\delta$ is the distance between the Fermi level and the bottom of the conduction band in the bulk; $\chi$ is the electron affinity energy with the lattice; and $V_D$ is the dipole component determining the potential drop due to molecules adsorbed onto the surface (herein RH $\approx 40\%$). For metals in air, Eq. (8) has the reduced form:

$$\Phi_{tip/sample} = \Phi_{bulk} + V_D.$$ 

By assuming the contribution of static charges for metals null, $V_0$ results:

$$V_0 = \frac{\Phi_{tip} - \Phi_{sample}}{-e} = \frac{\Phi_{tip,bulk} + V_D - \Phi_{sample,bulk}}{-e} = \frac{\Delta \Phi_{bulk} + V_D}{-e},$$

where $\Phi_{sample,bulk}$ is the work function of the reference sample whose properties do not depend on adsorption (Novikov & Timoshenkov, 2003); $\Phi_{tip,bulk}$ is the work function of the tip that is affected by the dipole layer $V_D$ (Mugo & Yuan, 2012).

Dipole drops $V_D$, as extracted from EFM-Phase measurements on the Au sample by using cantilevers with different conductive coatings, are: (i) $V_D = (0.11 \pm 0.03)$ eV and $V_D = -(0.47 \pm 0.03)$ eV for the Au tip, with $\Phi_{Au,bulk} = 5.1$ eV from the literature (Michaelson, 1977), and the Pt tip, with $\Phi_{Pt,bulk} = 5.65$ eV from the literature (Michaelson, 1977), respectively. These results are in agreement with the ones obtained in ref. (Mugo & Yuan, 2012) by Kelvin probe force microscopy; (ii) From the literature, the oxidation states of Co are CoO and Co$_2$O$_4$ with a work function, $\Phi_{Co,oxide}$, of 4.6 and 6 eV, respectively (Greiner et al., 2012). Accordingly, $V_D$ ranges from $\sim 0.4$ to 1 eV for the Co tip which agrees, for example, to the shift of surface potential observed for adsorbed hydrogen on Co films (Duš & Lisowski, 1976); and (iii) in literature, the work function of conductive diamond films used for AFM probe coatings,
Spatial resolution in EFM-Phase

In every experimental setup employing a scanning probe microscopy, an adequate modelling of the probe is fundamental. The most common assumption for such a probe in a real EFM setup is a macroscopic cantilever with a mesoscopic tip cone ending with a nanometre-sized apex, each one being predominant at a different surface-probe separation z[77–80].

As discussed by Belaidi et al. (1997), the total force $F(z)$ acting on the probe is the sum of forces acting on both the tip $F_{tip}(z)$ and the cantilever $F_{cantilever}(z)$. For large distances $z > 10 \mu m$, the cantilever contribution in $F(z)$ is dominant, as can be expected when the tip is far from the plane. On the opposite side, the tip apex dominates $F(z)$ at small distances (tens of nm) (Colchero et al., 2001), whereas the cone aperture $\theta$ and the cone length $L$ become the leading terms of $F(z)$ for intermediate $z$ (from tens of nm to µm).

Accordingly, the spatial resolution of EFM images $\rho$ will depend on $z$. As reported by Gómez-Moñivas et al. (Gómez-Moñivas et al., 2001; García & Pérez, 2002), $\rho$ depends specifically on both $z$ and the radius of curvature of the tip $r^1$ through the relation $\rho \approx \sqrt{z \cdot r}$. For a force gradient signal, like the phase $\psi_i(\omega)$ measured in EFM-Phase (see Eq. 6), $\rho$ ranges from $\approx 20$ to $\approx 30$ nm at very small distances $z (z \approx 10$ nm), whereas it broadens for increasing $z$.

Spectroscopic curves $\psi_i(\omega)$ vs $z$ are useful for assessing the spatial resolution $\rho$ for increasing bias voltage $V_{tip}$[82]. Relatively soft cantilevers coated by Pt, NT-MDT NSG11/Pt (resonant frequency $\omega_0 \approx 167$ kHz, quality factor $Q = 465$ and spring constant $k \approx 12.2$ N/m), are employed in spectroscopic measurements. The upper limit of the $z$ range, 2.3 µm, was determined by the microscope (SPM Solver Svena HV, NT-MDT, Zelenograd, Moscow, RU).

On the other hand, the determination of the lower limit needs firstly a combined analysis of amplitude $A$ vs $z$ and $\psi_i(\omega)$ vs $z$ spectroscopic curves (Fig. 3) with both sample and tip grounded. Out of the tip–sample interaction (z larger than point $e$ in Fig. 3), the cantilever oscillates freely with an amplitude $A_0$ and a phase $\psi_i$ of $\pi/2$, as expected for noninteracting tip. When the tip approaches closely the surface (z distances between points $d$ and $e$), the oscillation amplitude remains unchanged, whereas the phase $\psi_i$ starts to increase because of the attractive force (Van der Waals) established between the tip and the sample. At the point $d$, the tip starts to touch the surface and the oscillation amplitude $A$ is reduced linearly from $A_0$ to 0 having experience of an unstable region between the attractive (amplitudes above the unstable region, $1.75 < \psi_i < 2$) and the repulsive (amplitudes below the unstable region, $0.85 < \psi_i < 1.25$) regimes of the tip–sample interaction. The slopes of such linear reductions are similar and, for graphical purposes, are indicated by dashed-dotted-dotted line in the repulsive regions.

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1 As reported in datasheets, $r$ is 3.5 nm for Au and Pt tips, 40 nm for Co tips and 100 nm for cd tips, reduced to 10 nm on flat surfaces thanks to the nanometric roughness of the cd film.
The tip has experience of several surface forces when it interacts with the surface, e.g., adhesive forces (Leite et al., 2012), having short interaction distances, i.e., \( z \leq 20 \) nm, compared to electrostatic forces that have long interaction distances. A hemicycle of the cantilever free oscillation is \( A_0/2 \approx 2.6 \) nm, therefore, a height of the second pass \( H \geq 23 \) nm grants that \( \phi_i \) depends only on the electrostatic interactions.

Spectroscopic curves \( \phi_i(\omega) \) vs \( z \) for increasing tip voltage \( V_{tip} \) are performed on a grounded highly oriented pyrolytic graphite (HOPG), a sample granting high electrical conductivity and a topographically flat surface (Fig. 4A). Curves show an increased phase gradient \( d\phi_i/dz \) for increasing \( V_{tip} \) and decreasing tip–sample \( z \), whereas they collapse to \( \pi/2 \) for \( z > 2 \) \( \mu \)m. The dashed line in Figure 4(A), correspondent to a fixed height \( H = 40 \) nm of the second pass technique; (B) Representative fits of spectroscopic curves at 1.5, 3 and 10 V in the range 35 < \( z < 45 \) nm (only three fits are shown for graphical purposes). Fits are performed with Eq. (13), and the constant \( m \) appearing in the \( y \)-axis counts \((1.94)^{-1} \cdot 10^3\).

Fig. 4. (A) Spectroscopic curves \( \phi_i(\omega) \) vs \( z \) for increasing tip voltage \( V_{tip} \) performed on HOPG. Curves show an increased phase gradient \( d\phi_i/dz \) for increasing \( V_{tip} \) and decreasing tip–sample \( z \), whereas they collapse to \( \pi/2 \) for \( z > 2 \) \( \mu \)m. The dashed line corresponds to the fixed height \( H = 40 \) nm of the second pass technique; (B) Representative fits of spectroscopic curves at 1.5, 3 and 10 V in the range 35 < \( z < 45 \) nm (only three fits are shown for graphical purposes). Fits are performed with Eq. (13), and the constant \( m \) appearing in the \( y \)-axis counts \((1.94)^{-1} \cdot 10^3\).

...
some expansions in Taylor series around the height of the second pass \( H \) (see Appendix) and the \( \eta_{tip} \) definition in cartesian coordinates, the explicit equation of \( \psi_{i} (\omega) \) in cartesian coordinates is:

\[
\psi_{i} \approx \frac{\pi}{2} + \frac{Q}{k} \cdot \frac{1}{1 + i} \cdot 1.94 \cdot 10^{-3}V^2 \left\{ \ln \left( \frac{\xi_{int}}{\theta} - 1 \right) \right\}
\]

\[
\left( + 0.644 \cdot \ln (g) - 0.643 - \frac{t}{0.7} \right),
\]

\( (13) \)

where \( V = (V_{tip} - 0.05) \), i.e. an horizontal shift voltage of 0.05 V is present in agreement to the results reported elsewhere on HOPG and for an RH of \( \approx 40\% \) (Liscio et al., 2008). For graphical purposes, three representative fits are shown in Figure 4(B): 1.5, 3 and 10 V. The residual sum of squares (RSS) is used for evaluating the fit quality: an RSS value closer to 0 indicates that the model has a smaller random error component, and that the fit is useful for prediction. Spectroscopic curves show decreasing RSS for increasing \( V_{tip} \): (i) for \( 0 < V_{tip} < 2.5 \) V, phase data are progressively less dispersed and RSS decreases from 0.71 to 0.18 (see 1.5 V data in Fig. 4B); (ii) for \( V_{tip} \geq 2.5 \) V, RSS is reduced progressively from \( 6 \cdot 10^{-2} \) to \( 5 \cdot 10^{-5} \) (see 3 and 10 V data in Fig. 4B).

As calculated from the fitting parameter \( g \) of Eq. (13), \( \xi_{int} \) vs \( V_{tip} \) follows an exponential decay trend although, in principle, it should be independent from \( V_{tip} \) (Fig. 5). In the range \( 0 < V_{tip} < 2.5 \) V (not reported in Fig. 5), the number of electric field lines \( \xi_{int} \) is constant because of its relative error (from 70% to 45%). Such large error agrees to the phase data dispersion shown in Figure 4(B). For \( V_{tip} \geq 2.5 \) V, \( \xi_{int} \) has a characteristic decay voltage \( V_{p} = (1.7 \pm 0.2) \) V and the exponential decay saturates to a plateau of \( \xi_{int} \approx 13 \). The apex field-enhancement effect explains this trend: the electric field lines are bent in proximity of the tip apex generating effective boundary region of the electric field lines, which is progressively reduced for increasing \( V_{tip} \) up to the saturation value (Henson, 1984; Forbes et al., 2003). Consequently, the minimum spatial resolution achieved in EFM-Phase images also depends on \( \xi_{int} \).

The coordinates \( (\eta = 0, \xi_{int}, \theta = 0) \) are the projection of the parabolic tip \( \eta_{tip} \) onto the sample surface. By following the work of Patil et al. (2000), the radius of interaction \( \rho \) can be calculated from the projected area \( B \) of the tip, i.e. \( B = \pi \cdot \rho^2 \), onto the sample surface:

\[
B = 2\pi H \int_{1}^{\xi_{int}} \sqrt{\xi^2 - \eta_{tip}^2} \, d\xi.
\]

\( (14) \)

By changing conveniently \( \lambda = \xi \cdot \eta_{tip}^{-1} \), Eq. (14) becomes:

\[
B = 2\pi H \int_{\frac{\eta_{tip}}{\sqrt{\lambda}}}^{\frac{\xi_{int}}{\sqrt{\lambda}}} \sqrt{\lambda^2 - 1} \, d\lambda.
\]

\[
= \pi H^2 \int_{\frac{\eta_{tip}}{\sqrt{\lambda}}}^{\frac{\xi_{int}}{\sqrt{\lambda}}} \left[ \lambda \cdot \sqrt{\lambda^2 - 1} - \ln \left( 2\sqrt{\lambda^2 - 1} + 2\lambda \right) \right] \lambda \, d\lambda.
\]

\( (15) \)

Firstly, Eq. (15) is tested on the projection of the tip base onto the sample surface. As measured by SEM, the tip base radius is \( \rho \approx 2 \) µm, which corresponds to \( \xi_{int} \approx 100 \). Interestingly, this value corresponds to the minimum value obtained in the range \( 0 < V_{tip} < 2.5 \) V; here, the spatial resolution of EFM-Phase images is poor because the whole tip is involved in the electrostatic interaction. Moreover, the lower is the voltage \( (V_{tip} \to 0) \), the larger is the contribution in the electrostatic contrast of both the whole tip and the cantilever. The apex...
field-enhancement effect is more pronounced for \( V_{tip} \geq 2.5 \) V, improving the spatial resolution of EFM-Phase images \( \rho \) from \( \approx 300 \) to \( \approx 60 \) nm for 2.5 and 10 V, respectively (dotted line in Fig. 5 shows the saturation value of \( \rho \)). The characteristic decay voltage \( V_d \) (1.7 ± 0.2) V suggests a large enhancement of the spatial resolution for \( V_{tip} \) greater than \( \approx 4 \) V. These \( \rho \) values explain why EFM-Phase images show high spatial resolution even when the tip is positioned far away from the surface (\( H = 40 \) nm) and, notably, they agree to the spatial resolution obtained by using different tip models (Colchero et al., 2001; Dunaevskiy et al., 2012).

Equation (12) shows that the spatial resolution of the electrostatic images is improved if \( \eta_{tip} = \frac{1}{H} (H + r) \) tends to 1. This is possible by: (i) reducing the radius of curvature \( r \), for instance either by decreasing the metal coating thickness or choosing an alternative geometry or fabrication process leading to sharper tip apices (Nishijima et al., 1999); (ii) the height of the second pass \( H \) should be reduced for having higher phase gradient \( \Delta \phi /d z \); (iii) reducing \( V_{tip} \) and (iv) increasing the \( Q/k \) ratio which can be done by changing the shape parameters of the cantilever (Kawakatsu et al., 2002) or measuring electrostatic forces with Bimodal AFM (Albonetti et al., 2011; Garcia & Herruzo, 2012).

### EFM-Phase on SiO\(_x\) stripes: inhomogeneous charge distribution

EFM-Phase is used to investigate the charge distribution of silicon oxide nanometric stripes. The stripes were fabricated by local anodic oxidation of a native silicon oxide layer on a Si wafer, by means of an AFM (Dagata, 1997; Dagata et al., 1998). The tip (negatively biased) and the surface (grounded, \( p \)-type Silicon, \( n_i = 9 \times 10^{14} \text{ cm}^{-3} \)) are electrically connected through the water meniscus formed in a controlled environment (relative humidity \( RH = 55\% \), \( T = 25^\circ\text{C} \)). When a voltage pulse is applied (33 V for 100 µs) between the closely spaced tip and sample, an intense electric field is established, determining the growth of silicon oxide hillocks (Diggle & Vijn, 1976). Combining pulses and tip movement, stripes are fabricated with a controlled size, i.e. width 830 nm, length 3 µm and height \( h \approx 5 \) nm (see topographic images of Fig. 6A and B).

Differently from the previous examples in Sections ‘EFM-Phase measurements’ and ‘Spatial resolution in EFM-Phase’ with metallic surfaces, which exhibit a homogeneous charge density distribution, the stripes provide an interesting model substrate for the study of inhomogeneous charge density and the mapping of the local charge. By using scanning Maxwell stress microscopy, Dagata (1997) demonstrated that the local oxidation process yields trapping of positive charges (holes) in the oxide with a density several orders of magnitude larger (up to \( 10^{21} \text{ cm}^{-3} \)) than in thermal oxide. Such value exceeds the upper theoretical limit value (\( 2 \times 10^{18} \text{ cm}^{-3} \)) expected for very high electric field applied to an oxide a few nm thick.

|                | \( k \) (N•m\(^{-1}\)) | \( H \) (nm) | \( \frac{d^2C}{dz^2} \) \( \times 10^{-4} \) F•m\(^{-2}\) | \( V_{FB} \) (eV) |
|----------------|---------------------|--------|------------------------|-------------|
| Case 1 Substrate | 3.2                 | 238    | 5.4 ± 0.2              | (–0.04 ± 0.02) |
| Stripe          |                     |        |                        |             |
| Case 2 Substrate | 3.0                 | 203    | 5.1 ± 0.2              | (–0.34 ± 0.02) |
| Stripe          |                     |        | 4.5 ± 0.2              | (–0.46 ± 0.01) |

Note: Cantilever elastic constants are calculated by using the Sader method (Sader et al., 1999).

There is a correlation between the doping nature of the substrate and the charging effects: for \( p \)-type silicon substrate, holes are trapped, whereas for \( n \)-type silicon substrate, the oxide is neutral or negatively charged, as reported by Lazzarino (2002), who confirmed the neutrality of stripes fabricated on \( n \)-type silicon by using spectroscopic photoemission and low energy electron microscopy. The silicon oxide stripes can be, therefore, used for assessing the EFM-Phase resolution and the validity model described in Section ‘Spatial resolution in EFM-Phase’ in the case of a distribution of localized charges.

The density of trapped holes in micrometric stripes fabricated on \( p \)-type silicon is investigated by comparing the parabolic behaviour of \( \phi_i \) vs \( V_{tip} \) measured on the substrate and the stripes at the same height of the second pass \( H \), i.e. 40 nm. The fitting parameters extracted from the phase-voltage curve by using Eq. (7) are shown in Table 2. Based on these results can sort out the local oxide stripes into two groups: without and with trapped charges, hereafter case 1 and case 2, respectively. In particular, the measured phase values \( \phi_i \) of the phase-voltage curve are the mean values ± the standard deviation of one (case 1) or two (case 2) Gaussians distributions used for fitting the phase values distribution measured on \( 3 \) µm × 2 µm EFM-Phase images (see Fig. 6C and D and Supporting Information). In case 1, stripe and substrate have the same phase value, whereas in case 2, two different phase values for the stripe and substrate are obtained.

\( \text{SiO}_x \) stripes with charges (case 2) can be useful for proving the lateral resolution of EFM-Phase images. Due to the tip–sample convolution (Canet-Ferrer et al., 2014), the topographic cross-section of a \( \text{SiO}_x \) stripe is a trapezoid with the half of the bases difference of \( \approx 60 \) nm (see Fig. 6E – bottom plot). As calculated in Section ‘Spatial resolution in EFM-Phase’, this value corresponds to the spatial resolution of EFM-Phase images for \( H = 40 \) nm: hence, the substrate and the \( \text{SiO}_x \) stripe should be laterally distinguished in EFM-Phase images within \( \approx 60 \) nm (Labardi et al., 2020). As shown in Figure 6(E) – top plot, this is confirmed for \( V_{tip} \) equal to 3 and 5 V, in agreement to the dependence of the spatial resolution on \( V_{tip} \) (comparable results are obtained on smaller parallel stripes – see Supporting Information).
The tip–sample system is comparable to a metal-oxide-semiconductor (MOS) interface where the tip is the metal, the air plus silicon oxide layer is the oxide and the Si substrate is the semiconductor. The $c$ parameter of Eq. (7), i.e. $V_0$, can be associated with the flat-band voltage ($V_{FB}$) of an MOS structure, which is, by definition, the voltage that induces a zero-net charge in the underlying semiconductor. The flat band condition means $P = 0$ in Eq. (8), so Eq. (10) becomes:

$$
V_{FB} = V_0 = \frac{\Phi_{tip} - \Phi_{sample}}{-e} = \frac{\Phi_{tip, bulk} + V_D - (\Phi_{sample, bulk} - Q_t/C_{stripe})}{-e} = \frac{\Delta \Phi_{bulk} + V_D + Q_t/C_{stripe}}{-e},
$$

where $Q_t/C_{stripe}$ (in V) is the excess of charges (holes) trapped in the silicon oxide. If there is no charge present in the oxide or at the oxide–semiconductor interface, the flat band voltage simply equals Eq. (10). A flat-band condition is assumed in the region of the substrate around the stripes (i.e. no charges are trapped inside the native SiO$_x$ or at the Si/SiO$_x$ interface).

As shown in Table 2, case 1 has $V_{FB}$ constant and equal to $-(0.04 \pm 0.02)$ eV for both substrate and microstripe. In case 2, it decreases from $-(0.34 \pm 0.02)$ to $-(0.46 \pm 0.01)$ eV for substrate and microstripe, respectively. On the other hand, the parameter $b$ (capacitive term) is constant for case 1, whereas it increases passing from the substrate to stripes in case 2. At zeroth-order approximation, the tip–sample capacitance depends on the distance $D$ between the tip and the Si/SiO$_x$ interface, which is assumed as the reference interface.
Fig. 7. (A) Case 1: Strip and substrate phase voltage parabolas ($Q = 238$ and $k = 3.2 \text{ Nm}^{-1}$). Parabolas are overlapped and $V_{FB}$ coincides for the substrate and the stripe (Table 2); (B) Case 2: Stripe (cross) and substrate (square) phase voltage parabolas ($Q = 203$ and $k = 3.0 \text{ Nm}^{-1}$). $V_{FB}$ measured on the microstripe shifts towards less negative value respect to the one measured on the substrate (Table 2). This indicates the presence of trapped charges in the stripe. (C) Normalized phase versus voltage curves (substrate) and (D) normalized phase versus voltage curves (stripe). Equation (6) has been used for normalization.

On the substrate, $D = H + S_{native}$, where $H$ is the second pass height and $S_{native}$ is the native SiO$_x$ thickness ($\approx 2$ nm, relative dielectric constant $\varepsilon_r = 3.9$) (Lazzarino et al., 2002). Accordingly, $C_{substrate} > C_{0-substrate}$, where $C_{0-substrate}$ is the tip–sample capacitance that is increased by the dielectric slab of native silicon oxide.

On the microstripe, the grown oxide layer $S_{stripe}$ is clearly thicker [the relative permittivity of fabricated SiO$_x$ stripes is 5.2 (Schmuki, 1995)]; the 3/5 of the stripe thickness is grown overhead the native SiO$_x$ surface, whereas the remaining 2/5 is grown beneath the Si surface (Stiévenard & Legrand, 2006). As measured by AFM, the average height of stripes is 3 nm; hence, the average total thickness of microstripe is 5 nm. In line with the procedure adopted for the substrate, $C_{stripe} > C_{0-stripe}$ and $C_{0-substrate} > C_{0-stripe}$ because of $D_{substrate} < D_{stripe}$. By following inequalities, $C_{substrate} > C_{stripe}$ that agrees to the experimental results shown in Table 2 where the substrate parabola is more stretched with respect to the stripe parabola.

To understand $V_{FB}$ and $b$ trends, a simple model reported in the literature is used (Donolato, 1995; Donolato, 1996). The tip–sample system is schematized by point-like charge $q$ (acting as tip) located at a distance $z$ from the plane surface of a grounded semi-infinite semiconductor ($p$-type) covered by a thin oxide layer. If the bias is positive, holes (majority carriers) are repelled leaving behind the surface a space-charge region (depletion region) with a sharp boundary and a constant charge density. The total electrostatic force ($F_{el}$) between the tip and the sample is the sum of two forces; the attractive force due to the image charges ($F_i$, an attractive force pointing toward the sample is negative for convenience) and the force due to the depletion region ($F_{depl}$, a repulsive force is positive for convenience). The latter depends on the substrate doping concentration $n_i$. According to Diggle and Vijh (1976), the electrostatic forces acting between a $2V$ biased tip and a grounded sample with a doping concentration of $n_i = 9 \cdot 10^{14} \text{cm}^{-3}$ are $F_{depl} = 6 \text{ pN}$ and $F_i = 1.2 \text{ nN}$. Being $F_i$ always larger than $F_{depl}$ in this ideal system, the electrostatic force $F_{el}$ is always attractive. When the tip bias is negative, holes are attracted towards the surface, forming a thin layer of charge, which shields the bulk of the semiconductor from the external field, as it would happen for a metal. Here, the contribution due to the depletion region disappears so that $F_{el} = F_i$.

Figure 7 (A and B) shows $\phi_i$ vs $V_{tip}$ parabolas measured on the semiconductor substrate (dashed line) and on the SiO$_x$ stripes (dotted line) in cases 1 and 2. For the case 1, microstripe and substrate parabolas are overlapped because $V_{FB}$ does not vary within the experimental error (Fig. 7A). The lack of electrostatic contrast between the fabricated stripes and the
native SiO$_x$ hints the absence of trapped charges in the stripes and an easy polarizability of both native and fabricated SiO$_x$. Conversely, case 2 shows parabolas clearly shifted ($V_{FB\text{-stripe}} - V_{FB\text{-substrate}} = -(0.12 \pm 0.03)$ V). In the model described in references (Donolato, 1995; Donolato, 1996), this effect corresponds to a sizable increase of the $F_d$ contribution in the tip–sample force ($F_d$ is constant because of $V_{tip}$ is constant). A decrease in $F_d$ can be explained with a local increase of the dopant concentration, which increases the force contribution of the depletion region $F_{\Omega}$ (220 pN, 18% of the total force). This is a strong evidence for a bimodal distribution of doping concentration in the fabricated stripes made by o-SPL.

From the above considerations, the curves display an analogous $\varphi_i$ vs $V_{tip}$ behaviour for negative bias, where $F_d = F_i$ (accumulation region). In both cases, the negative parabola branches are overlapped. It turns out that in these measurements, the effect of the depletion region is negligible (only the 5% of $F_d$), and the main contribution for the asymmetry in the curve’s shape is due to the work function effect.

For positive bias, the phase measured on the microstripe decreases with respect to the phase measured on the substrate due to a decrease in $F_d$. This is particularly evident in case 2 (Fig. 7B). This effect causes a potential variation between substrate and stripe, i.e. $V_{FB}$, which results into an effective bias voltage ($V_{tip} - V_{FB}$) applied to the tip–sample system due to the presence of charges trapped into the stripe.

As a consequence, the stripes containing trapped charges show a phase dependence on the voltage that has lower $\varphi_i$ values in the right branch (positive tip bias) with respect to the left branch (negative tip bias). The branch asymmetry corresponds to the presence of more charges trapped into the silicon oxide or at the Si/SiO$_x$ interface.

In both cases, the curves obtained in the stripes and substrates are compared after normalizing them to the ratio $Q/k$ of the different cantilevers used in the experiments [Mikro-Masch, HQ:NSC36/Pt, Cantilever A: $\omega_0 = 142.97$ kHz and $k = 3.2$ N m$^{-1}$, Cantilever B: $\omega_0 = 152.41$ kHz and $k = 3.0$ N m$^{-1}$ with $k$ calculated with Sader method (Sader et al., 1999), see Supporting Information for SEM images of a typical EFM Pt tip]. It can be seen that the parabolas overlap to a universal curve by rescaling them with respect to the cantilever parameters $Q/k$ (Fig. 7C and D).

Figure 7(C) shows that the renormalized curves for the substrate are symmetric with respect to the tip bias polarity, residing in the same fitting parabola (dashed-dot-dot line). This is a relevant information because the capacitance of the depletion region induced in the semiconductor for positive voltages is, in principle, bias dependent. The symmetry ensures us that this effect is below our detection sensitivity. The direct comparison of the normalized stripes parabolas (Fig. 7D) shows that the parabola for case 2 (where charges are trapped) displays a lower force gradient, arising from a reduced curvature of the capacitance with respect to neutral microstripe (as indicated in Table 2).

In case 1, the parameter $b$ values extracted from Eq. (7) are constant within the experimental error (Table 2). This shows that the fabricated oxide stripe (case 1) and the native silicon oxide are easily polarizable. In case 2, the presence of trapped charges generates a space charge that contributes to the tip–sample capacitance (Grove et al., 1964), reducing $d^2C/dz^2$ in correspondence to the microstripe ($4.5 \pm 0.2 \times 10^{-4}$ F m$^{-2}$ with respect to the substrate value ($5.1 \pm 0.2 \times 10^{-4}$ F m$^{-2}$). Such a reduction is ascribable to an excess of holes $Q_i$ trapped inside the fabricated microstripe that causes an increase in $F_{\Omega}$ and, consequently, a decrease in $\varphi_i$ (Nishijima et al., 1999; Kawakatsu et al., 2002).

By assuming negligible interfacial traps and mobile charges in both native and fabricated SiO$_x$ (Donolato, 1995; Donolato, 1996), $Q_i = Q_{\text{stripe}} - Q_{\text{substrate}}$, where $Q_{\text{stripe}}$ is the charge accumulated on the microstripe and $Q_{\text{substrate}}$ the one accumulated on the substrate. From the definition of capacitance and Eq. (16), $Q_i$ is:

$$V_{FB\text{-stripe}} - V_{FB\text{-substrate}} = \frac{\Delta \Phi_{\text{bulk}} + V_D + Q_i/C_{\text{stripe}}}{-e} - \frac{\Delta \Phi_{\text{bulk}} + V_D}{-e} = -\frac{Q_i}{e \cdot C_{\text{stripe}}}. \quad (17)$$

Equation (17) can be resolved by calculating the capacitance of the tip–sample system on the microstripe $C_{\text{stripe}}$ referred to the Si/SiO$_x$ interface. In principle, it can be calculated as two capacitors in series: the tip–SiO$_x$ surface capacitor ($C_{\text{tip}}$) in the prolate spheroidal coordinate reference system and the SiO$_x$ surface–Si/SiO$_x$ interface ($C_{\text{int}}$) as a parallel plate capacitor. This assumption is correct if the electric field lines within the stripe, i.e. $\xi$ lines, are orthogonal with respect to the surface. In the prolate spheroidal coordinate reference system, the angle $\theta$ between the unit vector tangent to $\xi$ lines and the surface ($\eta = 0$) is:

$$\theta = \frac{\pi}{2} - \eta \sqrt{\frac{\xi^2 - 1}{\xi^2}}. \quad (18)$$

By considering EFM-Phase images with the best resolution, $\xi = \xi_{\text{int}} \approx 13$, Eq. (18) becomes:

$$\theta \approx \frac{\pi}{2} - \eta. \quad (19)$$

By definition, the distance between the tip and the sample is $z = n \cdot \xi \cdot \eta$ where $n$ is the foci distance $n = \sqrt{z(n + r)}$, therefore, Eq. (19) is:

$$\theta \approx \frac{\pi}{2} - \eta = \frac{\pi}{2} - \frac{z}{n \cdot \xi_{\text{int}}} = \frac{\pi}{2} - \frac{z}{\sqrt{z(n + r)} \cdot \xi_{\text{int}}}. \quad (20)$$

As described above, the fabricated SiO$_x$ stripes are, in average, 5 nm thick. Therefore, $z = 5$ nm and $r = 28$ nm. The electric lines emerging from the stripe surface have $\theta \approx \pi/2 - 0.03$ (i.e. 89.2°), that is, for practical purposes, $\approx \pi/2$. © 2020 Royal Microscopical Society, 280, 252–269
The tip–SiO$_2$ surface capacitor ($C_{tip}$) is calculated analytically in the prolate spheroidal coordinate reference system as (Momoh et al., 2009):

$$C_{tip} = \frac{4\pi \cdot n \cdot \varepsilon_0 (\xi_{int} - 1)}{\ln \left( \frac{4 + \rho \cdot \varepsilon_{0} \cdot r_{0}}{4 - \rho \cdot \varepsilon_{0} \cdot r_{0}} \right)}.$$  \hspace{1cm} (21)

In the second pass technique, $n_{tip} = \sqrt{H/(H + r)}$ with $H = 40 \text{ nm}$ and $r = 28 \text{ nm}$, $n = \sqrt{H/(H + r)}$, $\xi_{int} \approx 13$ and $\varepsilon_0 = 8.854 \times 10^{-12} \text{ F/m}$, obtaining a $C_{tip} = (34 \pm 3) \text{ aF}$. EFM-Phase images with the best resolution have $\rho \approx 60 \text{ nm}$, so $C_{ox}$ is:

$$C_{ox} = \frac{\varepsilon_0 \varepsilon_r B}{S_{stripe}} = \frac{\varepsilon_0 \varepsilon_r \pi \rho^2}{S_{stripe}},$$  \hspace{1cm} (22)

where $\varepsilon_r = 5.2$ for the fabricated SiO$_2$ (Schmuki, 1995) and $S_{stripe}$ is 5 nm, obtaining $C_{ox} = (104 \pm 12) \text{ aF}$. The capacitance of the tip–sample system on the stripe $C_{stripe}^{-1} = C_{tip}^{-1} + C_{ox}^{-1}$ giving $C_{stripe} = (25 \pm 4) \text{ aF}$.

By using Eq. (17), the amount of charge $Q$ trapped into the cylindrical region of the stripe with base $\pi \cdot \rho^2$ and height $S_{stripe}$ is $(3.0 \pm 0.5) \text{nC},$ equivalently, $(19 \pm 3) \text{ e}(1 \text{ e} = 1.602 \times 10^{-19} \text{ C}).$ This amount of charges corresponds to a trapped charges concentration of $(3.4 \pm 0.5) \times 10^{17} \text{ cm}^{-3}$ in agreement with the expected theoretical (Lazzarino et al., 2002) and experimental (Chiesa & Garcia, 2010) values. Moreover, it exceeds the doping concentration of the substrate (for $p$-type, $n_i = 1.1 \times 10^{13} \text{ cm}^{-3}$) correspond to a resistivity of $12 \Omega \cdot \text{cm}$.

Conclusions

An experimental protocol for obtaining quantitative electrostatic measurements by EFM-Phase is provided. By modelling the electrical interaction of a tip–sample system in a prolate spheroidal coordinate reference system, the minimum spatial resolution of EFM-Phase images for a second pass height $H$ of 40 nm is analytically defined and estimated to $\approx 60 \text{ nm}$, in agreement with the values reported in the literature. The spatial resolution is also correlated, for the first time, to the apex field-enhancement effect induced by the tip bias, explaining why EFM-Phase images show high spatial resolution even when the tip is 40 nm apart from the sample surface. This theoretical framework has been used to investigate both metal surfaces, with homogeneous charge distribution, and silicon oxide stripes fabricated by o-SPL, which instead exhibit an inhomogeneous charge distribution. By EFM-Phase, we have obtained surface potential information of micrometric-scale oxide features as a function of holes concentration within the growing oxide film. By applying the same procedure to stripes patterned on the same substrate, two types of stripes with and without, the relative amount of trapped charges can be quantified. The density of the trapped holes exceeds the doping concentration of the underneath Si, in agreement with previous experimental measurements. Nowadays, o-SPL enables the fabrication of several nanometric structures in a reproducible way (Ryu & Garcia, 2017), but without a precise control of the charges trapped during the patterning process. The application of the proposed analytical model to the control of the amount of charges trapped within superficial nanostructures during different nanomanufacturing processes enables us to envision the future high-resolution encoding of triboelectric information for emerging applications.

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Schematic diagram of the tip–sample geometry parameters used to model the surfaces of the tip and the sample in a typical EFM arrangement. The probe spheroidal coordinate system is particularly suitable for describing this system. It is given by

$$x = \eta \cdot \sqrt{(\xi^2 - 1)(1 - \eta^2) \cos \vartheta},$$

$$y = \eta \cdot \sqrt{(\xi^2 - 1)(1 - \eta^2) \sin \vartheta},$$

and

$$z = \eta \cdot \xi \cdot \vartheta, \text{ where } 1 \leq \xi \leq \infty, 0 \leq \eta \leq 1 \text{ and } 0 \leq \vartheta \leq 2\pi \text{ describe the permissible ranges of the coordinates } \xi, \eta \text{ and } \vartheta. \text{ The tip surface is assumed to be represented by a portion of hyperboloidal surface } \eta_{\text{tip}} = \sqrt{\xi/(\xi + r)}. \text{ Here, } z \text{ is the tip–sample distance and } r \text{ is the tip radius. The sample surface is the } x–y \text{ plane characterized by } \eta_{\text{sample}} = 0.$$

As reported by Patil et al. (2000), the infinitesimal contribution of the force along the z axis, \(F_z\), of a conducting tip interacting electrically with a metallic surface is:

$$d_F = -8\pi \varepsilon_0 V^2 \frac{\xi}{\left(\xi^2 - \eta_{\text{tip}}^2\right)} \cdot \ln^2 \left(\frac{1 + \eta_{\text{tip}}}{1 - \eta_{\text{tip}}}\right) \, d\xi.$$  \hfill (A1)

**Appendix**

Figure 8 shows two confocal hyperboloidal surfaces of revolution, which were used to model the surfaces of the tip and the sample in a typical EFM arrangement. The sample surface is the x–y plane characterized by \(\eta_{\text{sample}} = 0\). As reported by Patil et al. (2000), the infinitesimal contribution of the force along the z axis, \(F_z\), of a conducting tip interacting electrically with a metallic surface is:

$$d_F = -8\pi \varepsilon_0 V^2 \frac{\xi}{\left(\xi^2 - \eta_{\text{tip}}^2\right)} \cdot \ln^2 \left(\frac{1 + \eta_{\text{tip}}}{1 - \eta_{\text{tip}}}\right) \, d\xi.$$  \hfill (A1)

Fig. 8. Schematic diagram of the tip–sample geometry parameters used in the proposed analytical EFM-Phase model.
where the attractive force pointing towards the sample is, for convenience, negative. Equation (6) shows how the measured phase \( \varphi(\omega) \) is related to the gradient of the force along the \( z \) axis \( df_z/dz \). By using the chain rule:

\[
\frac{df_z}{dz} = \frac{df_z}{d\eta_{tip}} \cdot \frac{d\eta_{tip}}{dz}.
\]

The multiplicand can be readily calculated from the \( \eta_{tip} \) definition reported in Section ‘Spatial resolution in EFM-Phase’:

\[
\frac{d\eta_{tip}}{dz} = \frac{d}{d\eta_{tip}} \left( \sqrt{\frac{z}{z+r}} \right) = \frac{1}{2z \cdot \eta_{tip}} \cdot \frac{r}{(z+r)^2}.
\]

On the other hand, the multiplier needs a deeper analysis. By starting from Eq. (A1):

\[
\frac{df_z}{d\eta_{tip}} = -8\pi\varepsilon_0 V^2 \xi \frac{d}{d\eta_{tip}} \left( \frac{1}{(\xi^2 - \eta_{tip}^2) \cdot \ln^2 \left( \frac{1+\eta_{tip}}{1-\eta_{tip}} \right)} \right).
\]

The derivative of the function within parentheses is:

\[
\frac{d}{d\eta_{tip}} \left( \frac{1}{(\xi^2 - \eta_{tip}^2) \cdot \ln^2 \left( \frac{1+\eta_{tip}}{1-\eta_{tip}} \right)} \right) = \frac{2 \cdot \eta_{tip}}{(\xi^2 - \eta_{tip}^2)^2 \cdot \ln^2 \left( \frac{1+\eta_{tip}}{1-\eta_{tip}} \right)} - \frac{4}{(1-\eta_{tip}^2) \cdot (\xi^2 - \eta_{tip}^2) \cdot \ln^3 \left( \frac{1+\eta_{tip}}{1-\eta_{tip}} \right)}
\]

\[
= F(\eta_{tip}) + G(\eta_{tip}),
\]

where \( F(\eta_{tip}) \) and \( G(\eta_{tip}) \) are two functions introduced for mathematical purposes.

As described in Section Introduction, EFM-Phase images are acquired by double pass technique where, in the second pass, the tip is retracted at a fixed height \( H \) (~40 nm in SiO\(_x\) stripe experiments – see Fig. 8) above the surface and scanned along the recorded topographic profile with an applied voltage bias. The cantilever oscillates with a free amplitude \( A_0 \approx 4.4 \) nm, so the tip moves periodically its position from \( H + A_0/2 \) and \( H - A_0/2 \), i.e. 42.2 and 37.8 nm, respectively. The radius of curvature of Pt tips was evaluated by SEM images as \( r = (28 \pm 2) \) nm (see Supporting Information), therefore, \( \eta_{tip} \) ranges from 0.7753 and 0.7579 when it passes from the maximum to the minimum tip positions along oscillation cycles. In the prolate spheroidal coordinates, a different \( \eta_{tip} \) corresponds to a different tip shape; however, due to the negligible variation of \( \eta_{tip} \) (~2%), it can be considered unaltered along oscillation cycles.

For estimating the order of magnitude of \( F(\eta_{tip}) \) and \( G(\eta_{tip}) \) (see Eq. A5), \( \xi \) and \( \eta_{tip} \) have to be considered. As defined in ref. (Patil et al., 2000), \( \xi \) varies in the range \([1, \infty]\), whereas \( \eta_{tip} \) ranges from 0.7753 to 0.7579 in the experimental conditions adopted for EFM-Phase measurements (the tip is close to the dull tip shown in Fig. 8). As sketched by Pan et al. (2005), \( \xi \) has to be larger than 1.3 for including the radius of curvature of a dull EFM tip (\( \eta_{tip} \in [0.7753, 0.7579] \), see Fig. 8). Within these ranges, \( F(\eta_{tip}) \) and \( G(\eta_{tip}) \) have the same order of magnitude (Fig. 9).

By combining Eqs. (A2)–(A5), the gradient of the force along the \( z \) axis is:

\[
\frac{df_z}{dz} = \frac{df_z}{d\eta_{tip}} \cdot \frac{d\eta_{tip}}{dz} = -16\pi\varepsilon_0 V^2 \cdot \frac{r}{(z+r)^2} \cdot \xi \frac{d\xi}{dz}
\]

\[
= \left( \frac{1}{\xi^2 - \eta_{tip}^2} \frac{1}{\ln^2 \left( \frac{1+\eta_{tip}}{1-\eta_{tip}} \right)} \right) \frac{d\xi}{dz}
\]

\[
= \left( \frac{1}{\xi^2 - \eta_{tip}^2} \frac{1}{\ln^2 \left( \frac{1+\eta_{tip}}{1-\eta_{tip}} \right)} \right) \frac{d\xi}{dz}
\]

\[
= \left( \frac{1}{\xi^2 - \eta_{tip}^2} \frac{1}{\ln^2 \left( \frac{1+\eta_{tip}}{1-\eta_{tip}} \right)} \right) \frac{d\xi}{dz}
\]

\[
\int_{\eta_{tip}}^{\infty} \frac{\tau d\tau}{(\tau^2 - 1)^2} = -\frac{1}{2\cdot\eta_{tip}} \left[ \frac{1}{(\tau^2 - 1)} \right]_{\eta_{tip}}^{\infty}
\]

\[
= \frac{1}{2} \left[ \ln \left( \frac{\eta_{tip}}{\tau^2 - 1} \right) \right]_{0}^{\infty}.
\]

Fig. 9. Calculated graphs of \( F(\eta_{tip}) \), \( G(\eta_{tip}) \) and \( F(\eta_{tip}) + G(\eta_{tip}) \) for visualizing the relative weight of each function in Eq. (A5) in order to evaluate approximations.

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To solve the bottom integral of Eq. (A7), an upper integration limit \( \xi_{\text{int}} \) is set for allowing the integral (otherwise divergent) to converge. This integration limit also sets the \( \xi \) lines involved in the electrostatic interaction between the tip and the sample.

\[
\int_{\xi_{\text{tip}}}^{\xi_{\text{int}}} \frac{\tau d\tau}{(\tau^2 - 1)^2} = -\frac{1}{2} \cdot \frac{\eta_{\text{tip}}^2}{(\tau^2 - 1)} \bigg|_{\xi_{\text{tip}}}^{\xi_{\text{int}}} = -\frac{1}{2} \cdot \frac{\eta_{\text{tip}}^2}{(\xi_{\text{int}}^2 - 1)} - \frac{\eta_{\text{tip}}^2}{(1 - \eta_{\text{tip}}^2)}
\]

\[
\int_{\xi_{\text{tip}}}^{\xi_{\text{int}}} \frac{\tau d\tau}{(\tau^2 - 1)} = \frac{1}{2} \ln(\tau^2 - 1) \bigg|_{\xi_{\text{tip}}}^{\xi_{\text{int}}} = \frac{1}{2} \left[ \ln(\xi_{\text{int}}^2 - 1) - \ln\left(\frac{1 - \eta_{\text{tip}}^2}{\eta_{\text{tip}}^2}\right) \right]
\]

By integrating Eq. (A7) in \( \xi \), as described in Eq. (A8), the force gradient results:

\[
\frac{dF_z}{dz} = \frac{8\pi \varepsilon_0 V^2}{\eta_{\text{tip}}^2} \cdot \frac{r}{(z + r)^4} \cdot \frac{1}{\ln^2\left(\frac{1 + \eta_{\text{tip}}}{1 - \eta_{\text{tip}}^2}\right)}
\]

\[
\times \left\{ \frac{1}{\left[\frac{1}{\xi_{\text{int}}^2} \cdot \ln\left(\frac{1 + \eta_{\text{tip}}}{1 - \eta_{\text{tip}}^2}\right)\right]} \right\}
\]

\[
\left( \frac{\eta_{\text{tip}}}{\left[\frac{1}{\xi_{\text{int}}^2} - 1\right]} - \ln\left(\frac{1 + \eta_{\text{tip}}}{\eta_{\text{tip}}^2}\right) \right)
\]

Finally, Eq. (A9) is expressed in cartesian coordinates by using the \( \eta_{\text{tip}} \) definition:

\[
\eta_{\text{tip}} = \sqrt{\frac{z}{z + r}} \cdot \frac{dF_z}{dz} = \frac{8\pi \varepsilon_0 V^2}{\ln^2\left(\frac{1 + \eta_{\text{tip}}}{1 - \eta_{\text{tip}}^2}\right)} \cdot \frac{r}{(z + r)^4}
\]

\[
\left\{ \frac{1}{\left[ \frac{r}{z} \cdot \frac{1}{\xi_{\text{int}}^2} - 1 \right]} \right\}
\]

\[
\times \left( \frac{\eta_{\text{tip}}}{\ln\left(\frac{1 + \eta_{\text{tip}}}{\eta_{\text{tip}}^2}\right)} \right)
\]

\[
\left\{ \frac{1}{\ln\left(\frac{1 + \eta_{\text{tip}}}{\eta_{\text{tip}}^2}\right)} \right\}
\]

with SI unit of measure in N m\(^{-1}\).

In EFM-Phase measurements, the tip is retracted at a fixed height \( H \) above the surface and it oscillates around such height with a free amplitude \( A_0 \). Being it small \( (A_0 \approx 4.4 \text{ nm}) \), it is possible to expand some functions of Eq. (A10) in Taylor series around the lift height \( H \) normalized with respect to the radius of curvature \( r \), i.e. \( r/H \). Specifically:

\[
\sqrt{1 + \frac{r}{H}} < 1 \Rightarrow \sqrt{\frac{r}{H} + 1 + \frac{(\frac{r}{H} - \frac{1}{H})}{2 \cdot \sqrt{\frac{r}{H} + 1}} \approx \sqrt{\frac{r}{H} + 1}
\]

\[
\ln\left(\frac{r}{H}\right), 0 < \frac{r}{H} \leq 2 \Rightarrow \ln\left(\frac{r}{H}\right) + \frac{\frac{r}{H} - \frac{1}{H}}{2}
\]

\[
\ln\left(\frac{1 + \eta_{\text{tip}}}{1 - \eta_{\text{tip}}^2}\right) \cdot \eta_{\text{tip}} < 1 \Rightarrow \ln\left(\frac{1 + \left(1 + \frac{\eta_{\text{tip}}}{1 - \eta_{\text{tip}}^2}\right)}{1 - \left(1 + \frac{\eta_{\text{tip}}}{1 - \eta_{\text{tip}}^2}\right)^2}\right)
\]

\[
\approx \ln\left(\frac{1 + \eta_{\text{tip}}}{1 - \eta_{\text{tip}}^2}\right) \approx \ln\left(\frac{1 + \eta_{\text{tip}}}{1 - \eta_{\text{tip}}^2}\right)
\]

The \( \eta_{\text{tip}} \) notation is used in the third expansion of Eq. (A11) for mathematical purposes. First and third series are constant in the \( r^{-1} \) range \([0.664, 0.741]\) with a relative error of 2\% and 6\%, respectively.

By using Taylor expansions of Eq. (A11) in Eq. (A10), the force gradient results:

\[
\frac{dF_z}{dz} \approx \frac{r}{z} \cdot \frac{1}{\ln^2\left(\frac{1 + \eta_{\text{tip}}}{1 - \eta_{\text{tip}}^2}\right)} \cdot \frac{8\pi \varepsilon_0 V^2}{\ln^2\left(\frac{1 + \eta_{\text{tip}}}{1 - \eta_{\text{tip}}^2}\right)} \left\{ \frac{r}{z} \cdot \frac{1}{\xi_{\text{int}}^2 - 1} - 1 \right\}
\]

\[
+ \left[ \frac{1}{\ln\left(\frac{1 + \eta_{\text{tip}}}{1 - \eta_{\text{tip}}^2}\right)} \right]
\]

satisfying the convenience that an attractive force pointing toward the sample is negative and its derivative is positive.

### Supporting Information

Additional supporting information may be found online in the Supporting Information section at the end of the article.

**Figure S1**: Typical topographic (a) and EFM-phase (b, in degree) images of the polycrystalline Au film.

**Figure S2**: Phase distribution \( \varphi \) (in degree) of the EFM-phase image. The distribution is fitted with a Gaussian distribution (dashed line).

**Figure S3**: Phase distribution \( \varphi \) (in degree) of the EFM-phase images on SiO\(_x\) stripes without (top plot) and with (bottom plot) charges.

**Figure S4**: SEM images of an EFM Pt tip (left image) and zoom of the tip apex (right image).

**Figure S5**: Topographic image of parallel stripes (a) and corresponding phase images (in degree) from 1 V (b) to 5 V (d). Topographic profile (e – bottom plot) and phase profiles (e – top plot).