Surface potential studies using Kelvin force spectroscopy

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Abstract. A home-built Kelvin force microscope combined with a spectroscopic method is dedicated to local measurements of topography and contact potential differences (CPD). This technique is based on a simple modification of a non-contact atomic force microscopy (nc-AFM), where a bias voltage is applied between the sample and tip during the CPD measurement. The changes in CPD between the tip and various sample materials have been measured. Kelvin force spectra of Pd/Si and of self-assembling monolayer films (SAMs) are presented.

The Kelvin method [1] is a well-established technique for measuring the contact potential differences (CPD) between a reference electrode and a sample. The CPD for clean metal surfaces is given by the difference in the work functions of the two materials. A common method of measuring the contact potential difference is the vibrating capacitor method or Kelvin method. In this method, the probe, which is made of a material with a known work function (commonly tungsten or platinum), is arranged close to the surface to be measured as a parallel plate capacitor with small spacing. In a simple model, the contact potential between the two materials is $V_{\text{CPD}} = 1/e(\Phi_2 - \Phi_1)$, where Φ_1 and Φ_2 are the work functions of the conductors, including changes due to adsorption layers on the surface. A periodic vibration between the two plates at frequency ω with amplitude d_1 results in a current $i(t)$ given by

$$i(t) = \frac{\partial C}{\partial z} \cdot (V_{\text{bias}} + V_{\text{CPD}})\omega d_1 \cos \omega t$$

where V_{CPD} is the contact potential difference, $\frac{\partial C}{\partial z}$ is the derivative of the capacitance of this plate capacitor, and the V_{bias} is the bias voltage applied between the tip and sample. The technique is to detect the zero point of current function $i(t)$ while the additional bias voltage is applied between the two plates until the electric field in between disappears, thus the contact potential difference $V_{\text{CPD}} = -V_{\text{bias}}$ can be measured. The Kelvin method has a high sensitivity for potential measurement but integrates over the whole plate area and does not provide a lateral image of the variation of CPD on the surface [2].

The local information about surface topography and CPD measurements can be achieved by using Kelvin force spectroscopy (KFS) [2–4]. The principle is similar to that of the Kelvin method, except that forces are measured instead of currents. An additional voltage is applied between tip and sample until the electric field in between vanishes. The force gradient is proportional to the change amplitude of the vibration, caused by the applied voltage. In KPS, the distance between the tip and sample is kept constant during the spectroscopic measurement.

In this work, local CPDs of various metal surfaces and various SAM-modified Au films relative to the Si probing tip
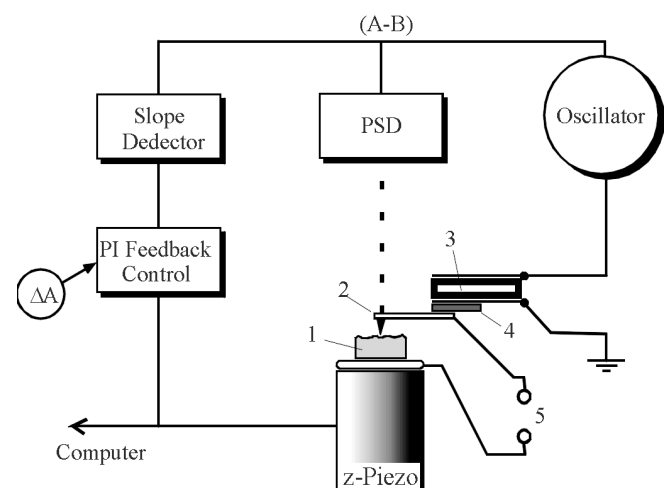

Fig. 1. Block diagram of KFS. 1, sample; 2, n-doped Si tip; 3, ac-piezo; 4, insulating layer; 5, dc bias voltage

are determined by using KFS, while the topographic informations are detected simultaneously.

1 Experimental

A home-built Kelvin force microscope [5] is used for this study. Figure 1 contains the block diagram of our KFS. A microfabricated single crystal Si cantilever (n-doped) of rectangular shape with a normal spring constant c_n typically of about 25 N/m and resonance frequency f_{res} of about 150 kHz, are used. The measurements were performed with an nc-AFM [6] with the beam deflection method [5]. The quality factor in the ambient condition is typically about 100. Therefore slope detection (also referred to as the amplitude modulation (AM) technique) is suitable for detection of the motion of the cantilever, where the cantilever tip is vibrated close to the surface to be measured. A feed-back loop is used to maintain a constant force gradient (for topographic imaging in non-contact mode), and an extra dc voltage is applied to the tip with the sample being grounded. The electrostatic force between the tip and the sample can be written as

$$F = \frac{1}{2}(U + U_c)^2 \frac{\partial C}{\partial z}$$

where U, U_c, C and z are the applied voltage, the contact potential difference, the capacitance, and the distance between the tip and the sample, respectively. Two methods are possible to determine the CPD:

– the second feedback loop technique,
– the spectroscopic method.

In the second feedback loop technique a sinusoidal voltage signal ($U = U_0 + U_s \sin \omega t$) is superimposed on the tip bias, in the absence of any surface or dielectric charge, the electrostatic force may be approximated as [7–9]

$$F = \frac{1}{2}(U_c + U_0 + U_s \sin \omega t)^2 \frac{\partial C}{\partial z}$$

The cantilever is driven by a sinusoidal driving force with constant frequency $f_{res} + \Delta f$ (slightly off resonance, Δf being typically 1–2 kHz) and amplitude. The cantilever resonance shift is detected indirectly from its vibration amplitude variation and used in the nc-AFM mode to control the distance between the tip and the sample. A second feedback loop is used to measure the CPD by nulling the electric field between the tip and the sample ($U_0 = -U_c$), while the distance in between was kept constant. The surface potential difference between the tip and the sample material is determined by controlling the tip bias voltage to make its surface potential equal to the sample material surface potential. The CPD between the tip and the sample material can be defined as the voltage applied to the tip when the electrical field in between disappears.

Instead of using a second feedback loop for the determination of CPD, a spectroscopic method is used: nc-AFM is applied to control the distance between the tip and the sample. On selected spots, the x-y movement is stopped, the feedback disabled by computer control and a amplitude vs. voltage curve is acquired. Afterwards, the x-y movement is contained in the normal nc-AFM mode. In contrast to the second loop technique, the spectroscopic method allows the user to determine not only the local CPD but also the local electrostatic force by varying dielectric properties and van der Waals
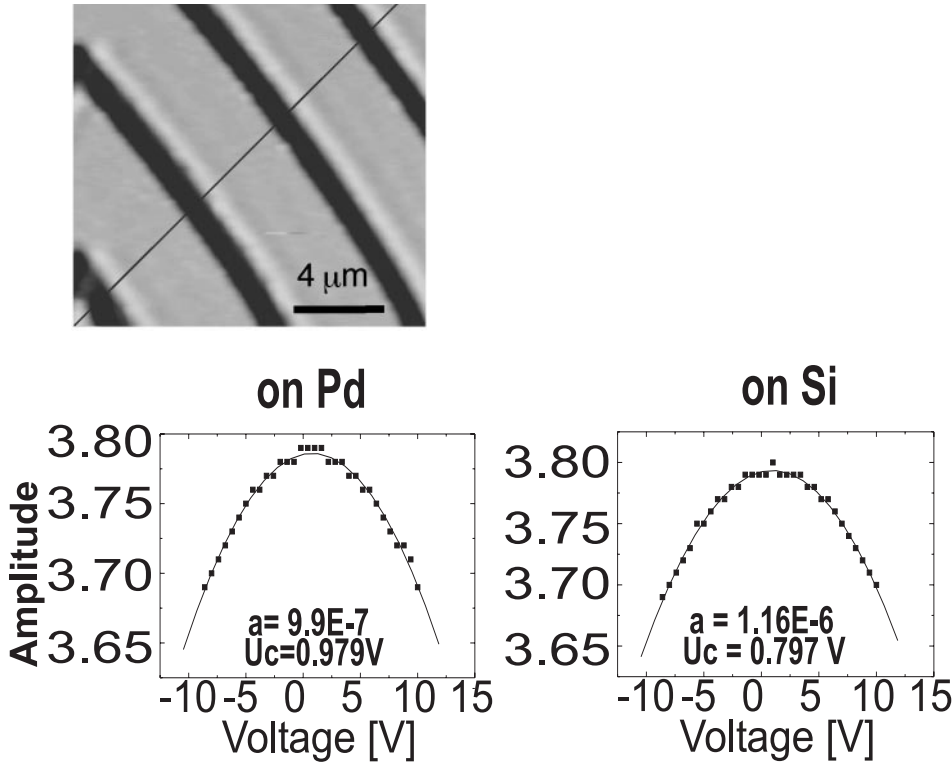

on Pd

a= 9.9E-7
Uc=0.979V

on Si

a = 1.16E-6
Uc = 0.797 V

Fig. 2. a Topographic imaging. **b** CPD measurements on Si/Pd using a n-doped Si tip
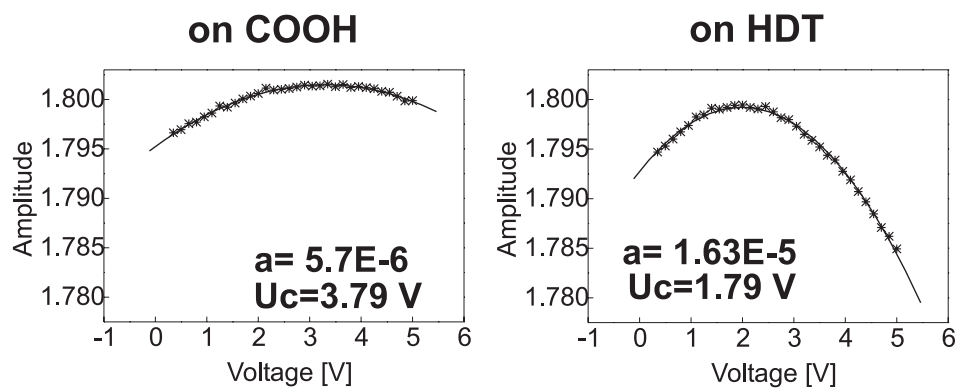
on COOH

on HDT

Fig. 3. CPD measurements on SAMs using a n-doped Si tip

forces. The minimum detectable potential different is given as

$$\Delta V = \sqrt{\frac{2k_B T \, kB}{\pi^3 Q f_0}} \frac{d}{\varepsilon_0 V_s R}$$

where k_B is the Boltzmann constant, T is the temperature, k is the cantilever spring constant, B is the instrument bandwidth, Q is the the cantilever quality factor, f_0 is the cantilever resonance frequency, d is the tip-to-sample distance, ε_0 is the dielectric constant of the vacuum, and R is the tip radius [10].

2 Results

Figure 2 shows topographic and CPD measurement of a Pd/Si sample. In the amplitude vs. substrate potential plot, a parabolic dependence is shown, since the electrostatic force is proportional to the square of the bias voltage. The solid line represents a second-order polynomial fit of the data, which indicates that the electrostatic force gradient is voltage dependent as shown in the following equation

$$\frac{\partial F}{\partial z} = a(U + U_c)^2 + c$$

where a is the curvature of the parabola which depends on the derivative of the effective capacitance ($a \approx \delta C/\delta z$), c is an offset due to the other forces, such as van der Waals force and other chemical forces, and U_c is the CPD value. The fit parameters for Si and Pd are found to be different, as shown in Fig. 2, the CPD value for palladium is large than that for silicon, which are in qualitative agreement with the theoretical value, whereas the curvature for Si is larger than that for Pd. However, since the measurements have been conducted under ambient conditions, it must be pointed out that for most materials a direct correlation with work function should not be expected. However, Si with native oxide is hydrophilic and is the material used for the tip. Accordingly, CPD values obtained in the N_2 chamber were more reproducible and stable than values obtained in air. The comparison between Si and Pd shows larger drifts of CPD on Si. Apparently, Pd is less affected by humidity. The variation of the curvature a and offset c are related to the different interaction volumes due to geometric effects.

In order to exclude geometrical effects, we selected heterogeneous surfaces with no topographic variation: SAMs were deposited with the polymeric stamping technique [11].

Since the method does not require a conducting sample surface, these thin insulating films can also be investigated. Figure 3 shows CPD measurements on a SAM-modified Au substrate using a n-doped Si tip. The CPDs of methyl-terminated substrate are found very stable over a long period ($U_c = 1.79$ V), whereas CPDs for carboxyl acid-terminated drifted substantially over the same period ($U_c = 3.79$–4.40 V). We conclude that the inert methyl-terminated surface is less affected by moisture than the hydrophilic acid-terminated surface is, where water and other contaminations preferentially absorb.

Force sensor n-doped Si tip can therefore be used in KFS to distinguish between different metal surfaces or between different SAM terminal groups. Thus chemical proporties and topographic information can be obtained simultaneously. Future investigations, such as the implementation of chemically modified tips, will reveal further possibilities with this sensitive spectroscopy.

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