Truncated-cone SPM tips for surface-molecules interaction studies

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Abstract

A new technique for the production of special shaped SPM tips is reported. Noble metal coated tips are produced with flat and circular tip front. The unusual truncated-cone tip shape is obtained by modifying commercial tips. The diameter of the tip front flat area can be varied continuously in the range $0.05 \div 1 \, \mu \text{m}$.

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I. INTRODUCTION

Since the breakthrough of the scanning probe microscopies \(^1\text{2}\) (SPM), an important step in their evolution was the tip production, whose important features are the availability of a good sharpness and the possibility to obtain reproducible mechanical and electric characteristics. It is well established that the use of such tips in a Scanning Tunneling Microscope (STM) or in an Atomic Force Microscope \(^3\) (AFM) allows imaging solid surface topography down to the atomic resolution. In particular AFM is made in order to be sensitive to forces of the nano-Newton order acting between the tip and the surface of a sample. The tip can move very close to the sample in vacuum, in air or immersed in a liquid \(^4\). Using AFM in air at room temperature, a layer of water is often condensed on the surface under investigation. Following the literature, this layer of water is the most important source of the attractive force experienced by the tip when it approaches the surface (snap-in) and when it is removed from the surface (snap-back). The forces acting on a tip when it is immersed in several liquids are extensively studied in order to achieve a better understanding of the liquid film influence on the imaging process \(^5\). In particular, adhesion and friction studies in presence of a liquid film on the surface are possible by measuring the torque applied to the scanning tip. The ability of the AFM apparatus to reveal forces in the nano-Newton range can be used to study the interaction between molecules and surfaces and to test the mechanical features of fluids in small volumes. Usually forces between surfaces are measured by means of the so called Surface Force Apparatus \(^6\): the involved surfaces are essentially two crossed cylinders and the area of contact between them is in the centimeter range. Using AFM with modified cantilevers, i.e. attaching micrometer spheres to levers, the contact area is reduced to the micrometer range \(^7\). In both the previous cases the geometry of the system is equivalent to a sphere interacting with a flat surface, with contact areas always larger than 1 \(\mu\text{m}^2\). In our opinion, a better insight on molecular forces acting in molecular layers of fluids on solid surfaces can be reached using tips having suitable shapes and/or decreasing the contact areas down the sub-micrometric scale. An appropriate shape could be flat surface parallel
to a solid surface (Fig.1). This kind of tip could be used to investigate the elastic properties of micrometric objects, besides modulating the interaction force, varying also the size of the contact area between the involved surfaces.

A more complete knowledge of the elastic properties of the materials at small scale has a great importance for instance in the study of liquid crystals (LC). The LC macroscopic behaviour is highly influenced by the order condition imposed by the surfaces. The interaction between the surface and the LC can cause spontaneous orientations of the LC molecules that influence the bulk molecules orientation \[8\]. Physical explanations of such processes are not well understood and the existing models are essentially macroscopical and phenomenological. The elastic energy stored in a LC sample is expressed as the sum of a term involving the energy stored in the volume related to the molecular texture in the bulk and a term regarding the interaction of the molecules with the surface (anchoring energy). Measurements on the elastic properties of the LC films can give informations on the internal structure of such films and on the strength of the anchoring conditions. Previous observations \[9,10\] were made using a Scanning Force Apparatus on nematic and smectic LC, measuring different kinds of forces, each reflecting a type of ordering of the LC film near the surfaces and the influence of the film thickness on such forces. An AFM with modified tips gives the possibility to investigate the same properties locally using surfaces with dimensions in the micrometer range, having also the possibility to modify these surfaces in order to give different anchoring conditions. It is possible to induce an anisotropy on the tip surface or to cover the tip itself with some material to induce homeotropic alignment in LC molecules.

In the present work, we focus our attention on the possibility to produce a new kind of tip having a flat surface which can be moved respect to a fixed one, recording the interaction forces. This result is obtained by means of a tip with a truncated cone shape, with a flat front surface whose area varies from \(2.5 \times 10^{-3}\) to \(1 \mu m^2\). Putting this modified tip in a scanning SPM apparatus, it is possible to operate in both compression and scanning mode in order to reveal, for instance, the response of a fluid to compression, viscosity and friction. Furthermore, it is possible to record the influence of an applied voltage between the tip and
the fixed surface. In the following we describe the method to shape commercial tips in a truncated cone fashion. This is achieved by coating a Si tip with a thin film of noble metal. A similar tip treatment was carried out by H. Andoh et al.; they developed a new tip fabrication technique consisting in the evaporation of a thin metal layer on STM tips, in order to provide a nanoscale deposition method with different metal species. We use, with a different purpose, the same metal deposition technique, adding a new feature: the change of the tip morphology, treating it to flatten the front end. The first step is performed in vacuum, using the evaporation system described in the next paragraph. The final tip treatment is carried out directly in the SPM apparatus (Fig.1). Force diagrams for standard and flat tips are reported for comparison.

II. TIP TREATMENT

A physical vapour deposition (PVD) system with a film thickness control is used for the deposition of Ag or Au on standard Si tips. Our coating unit consists of a glass chamber (46 cm diameter and 52 cm height) for ultimate vacuum down to \(10^{-6}\) mbar. The vacuum is achieved in two steps: rough vacuum until the pressure of \(10^{-2}\) mbar by a mechanical rotary pump and the final high vacuum by a turbomolecular pump. The coating material is heated in a suitable evaporation oven by Joule effect. In our case, the typical working temperature of the evaporation source is around 1400 °C, where Ag (or Au) sublimates and its vapor deposits on the tip, placed in front of the oven. In order to avoid thermal deformation of the cantilevers due to irradiation, tips are placed at a minimum distance of 30 cm from the evaporation source and a stainless steel shutter with a pin hole is interposed between the tip and the oven (Fig.2). The film thickness is monitored by means of an oscillating quartz balance: the oscillating frequency of the quartz crystal changes when a film is deposited on the quartz substrate itself. The deposition rate, during the coating process, is fixed at about 1 Å/s and is controlled by means of a rate meter. After the coating, the tip is introduced in an AFM apparatus. The AFM used for our work is an Autoprobe CP by Park Scientific.
Instruments with a 10 \( \mu m \) scanner. Typical AFM tips are placed on the edge of a triangular cantilever, whose deflection (due to the force between the tip and the sample) is revealed by an optical system. The optical control is essentially a laser beam, that hits the back of the cantilever and is reflected towards a photosensitive detection system (PSPD). Normally, the tip is rastered on the sample surface in order to depict its topography through the cantilever deflection revealed by the PSPD signal. We used the scanning apparatus to move a Si tip coated with the Ag (or Au) thin film on a Si(111) atomically flat wafer, in order to deform the metal covered tip front. The tip is pushed against the Si substrate with a quite high constant force and the rastering is performed in constant force mode. In this case, a feedback circuit permits to adjust the cantilever position to keep its deflection constant. We have found the following optimized values for the scan parameters to produce good truncated-cone tips: rastering on a 4 \( \mu \)m x 4 \( \mu \)m area, rastering frequency below 4 Hz, applied force in the 100 nN range and rastering time from a few minutes to 1h, when the Ag (or Au) film thickness is a few hundred Å. The tip front radius depends both on the combinations of deposited material thickness and on the applied force and, at present, must be checked for each tip.

III. TIPS CHARACTERIZATION

The tip shape is monitored by a scanning electron microscope (SEM) at the different steps of treatment. A commercial AFM tip from Park Scientific Instruments is imaged in a SEM picture shown in Fig.3. It has a high aspect ratio and curvature radius lower than 20 nm. The cantilever is attached to a Si chip and its length is about 180 \( \mu \)m. After the Au deposition the aspect ratio remains high and the curvature radius is now about 0.2 \( \mu \)m (see Fig.4). The deposition is quite uniform and no bumps are usually revealed in SEM pictures. Fig.5 shows the SEM picture of an Au coated tip having the flat area diameter of about 0.3-0.4 \( \mu \)m. A further characterization is achieved by scanning a freshly Ag coated tip on a calibration grid. Direct information on the tip shape can be obtained from the
image analysis of grid data. The apparent size of determined grid features can be related to the tip radius, that, in the case of a typical truncated tip, can be estimated about 700 Å. Assuming that the radius of curvature of a commercial tip is about 100 Å, it follows that the Ag coating layer is about 600 Å thick, in agreement with the quartz balance reading.

IV. TEST MEASUREMENTS

In order to compare the different behaviour of a truncated cone tip with a sharp one, we acquired a set of force vs. distance curves on a wafer of atomically flat Si(111) surface at room temperature and 50% of relative humidity [14]. Forces vs. distance curves [15,16] are plots of the vertical forces between the tip and the sample as the z-scanner extends and retracts in a fixed x-y point. These curves can be acquired controlling various parameters such as the range of extension of the piezo tube (from 0 to 5.564 µm), the number of acquired points (from 5 to 2048) and the sweep time (from 0.1 to 600 seconds). Data from consecutive scan can be averaged to generate a curve with a lower noise-to-signal ratio. The curve in Fig.6 is taken with a commercial tip in a z range from 0 to 2.782 µm, using two seconds per sweep and without data averaging. In Fig.7 we show a curve taken with the Ag coated tip with flat end in the same conditions as the previous one. The two curves show quite similar features. When the scanner starts its path toward the surface, the cantilever feels no forces, so it is extended until it experiences the van der Waals attractive force (snap-in point) and the tip comes in contact with the surface. If we continue to extend the scanner, the tip feels the force due to the tip-surface repulsion. When the scanner begins to retract, the force follows a different path, both in the repulsive part, owing to the nonlinearities of the z piezo tube [17], and in the attractive part owing to capillary forces due to a thin water layer of the sample surface. The scanner retracts until the tip is separated from the water layer (snap-back point) and a zero-force condition is recovered. It’s worth noting that the upper and lower limits of the curves are cut off, this is due to the saturation of the electronics of the system. From a comparison between the curves shown in Figs.6 and 7, we
can observe that in the retraction path of a flat end tip the snap back feature takes places at a greater distance from the surface than in the commercial tip curve. The typical elastic constant range of the cantilever is 0.01-0.5 N/m. We suppose that the elastic properties of the cantilever itself are unchanged by the coating because the thickness of the deposited film which is small with respect to the cantilever thickness and to the deposition method, that gives a non-compact Ag (or Au) film. Nevertheless the cantilever mass increases changing its inertial properties. This does not influence the force measurements that can be considered quasi-static.

V. INTERACTION FORCES

As already noted, the snap-in feature is caused by the van der Waals interactions between the tip and the sample. We can analyze the London-van der Waals interaction forces by modeling the tip as shown in Fig. 8. It consists of a conical section, which surround the entire Si tip (a commercial AFM ultralever tip with a cantilever spring constant equal to 0.26 N/m), followed by a spherical crown surface and the front flat surface. Owing to cantilever deformation due to irradiation and to mechanical adjustements during the flattening process, the conical section of the tip is not perpendicular to the substrate. It is reasonable to assume that the principal contribution to the total force on the probe is due to the spherical and flat sections whose parameters are the radius of the sphere $R$ and the two angles $\alpha$, $\beta$. The expression for the total London-van der Waals interaction force between a plane substrate and the coated tip can be obtained using the method described in [18] and is given by

$$F_z(d) = F_{zs}(d) + F_{ss}(d),$$

where the contribution of the flat surface is

$$F_{zs}(d) = \frac{-AR^2 \sin^2 \alpha}{6d^3},$$

where $A$ is the non retarded-Hamaker constant [19] and $d$ is the separation between the tip and the surface. The contribution of the spherical surface is
\[ F_{zs}^{ss} = -\frac{A}{6} \left\{ \frac{R \cos \alpha - d}{d^2} + \frac{d + R(\cos \alpha - 2 \cos \beta)}{[d + R(\cos \alpha - \cos \beta)]^2} \right\}. \] (3)

By making \( \alpha = 0 \) and \( \beta = \pi \) in the above expression we obtain the expression for the force-distance relation for a spherical tip

\[ F_{zt}^{st} = -\frac{2AR^3}{3d^2(2R + d)^2}. \] (4)

We apply this analysis of the force-distance relations to one set of experimental data obtained from a Ag coated truncated-cone probe interacting with a flat Ag sample in order to determine the Hamaker constant. From the SEM image of the coated tip we obtain a tip radius at \( R = 161.28 \) nm, and the angles \( \alpha = 0.378 \) rad and \( \beta = 1.292 \) rad. The spring constant of the cantilever is fixed at 0.26 N/m.

One of major problem in AFM experiments is the determination of the point of the zero force and zero separation. We fit each force curve to a function of the form

\[ F^m(d) = F_{vdW}(d + d_0) + B \times (d + d_0) + C, \] (5)

where \( F^m \) is the measured force, \( F_{vdW} \) is the London-van der Waals force and the second term represents a linear background (\( d_0 \) is the absolute plate separation and \( B \) and \( C \) are constants). The best fit values of \( B, C, \) and \( d_0 \) are determined by minimizing the \( \chi^2 \) and these values are used to subtract the systematic errors from the force curve in a region \( 5 \leq d \leq 80 \) nm and obtain the measured London-van der Waals forces as

\[ F^m_{vdW}(d) = F^m(d) - Bd - C. \] (6)

The fitted Hamaker constants for 17 different scans ranges from 64 to 183 zJ and its best estimate is 111.3 ± 19.4 zJ. The Hamaker constant for a gold coated AFM probe on a flat gold surface was obtained by Rabinovich and Churaev [20] to be in the range from 90 to 300 zJ and by Argento and French [18] to be 126 zJ.

Fig. 9 shows the experimental data and the fitting obtained with our analysis for one single scan. The curve plotted is in good agreement with the experimental data.
The snap-off features are governed by the capillary forces. This kind of interaction is strictly related to the properties of hydrophilicity of the involved surfaces and the water layer thickness. We do not give a model for the capillary forces in our case because we cannot determine the water film characteristics and, thus, we miss a fundamental parameter for the force analysis. The commonly used model [6] that describes the capillary force is not useful because it regards the interaction of a curved surface with a flat one, while we have two flat surfaces. Intuitively, we expect to have increasing capillary force with the radius of the flat tip, but not in proportion respect to the curvature radius of a commercial tip.

VI. CONCLUSIONS

We describe the production and test of truncated cone shaped tips. A noble metal film, deposited on commercial tips, is shaped by pushing them with a constant force on an atomically flat Si(111) wafer in air. The film thickness and the applied force are the main parameters in the front radius control. We make a first attempt to describe the van der Waals interaction forces between the tip and the sample. A comparative test on the capillary forces acting on a normal tip and on a flat front tip, shows a clear increase in the latter case.

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FIG. 1. In a) is shown a sketch of a typical commercial tip with a sharp end partially immersed in the layer of water that is often present on surfaces in air. b) With new truncated-cone tips, we can have a better insight on forces acting in molecular layers between the tip and the sample. Graphic scheme of the treatment to shape a tip in a truncated cone fashion: c) initially we have the typical sharp tip, d) after we coat it with a thin layer of a noble metal and e) finally we obtain the truncated cone shape by rastering the tip on the atomically flat surface of a Si(111) sample.
FIG. 2. a) In this SEM picture is shown a lateral view of PSI cantilevers before the noble metal coating. b) Cantilever deformation due to irradiation, when tips are placed too close (about 10 cm) to the evaporation source.
FIG. 3. *SEM picture of a PSI ultradev lever tip.*
FIG. 4. *SEM picture of an Au coated ultralever tip.*
FIG. 5. Au coated ultralever tip flattened after several scans on a Si(111) substrate in an AFM system.
FIG. 6. Force vs. distance curve of a commercial tip on a Si(111) substrate. A and B are respectively the snap-in point and the snap-back point.
FIG. 7. Force vs. distance curve of a silver coated tip on a Si(111) substrate with A and B respectively the snap-in and snap-back points. Its worth noting that the attraction mainly due to capillary forces are bigger than that shown in the previous picture.
FIG. 8. Model adopted for coated tip-sample system. $R$ is the radius of the spherical part of the probe, $\alpha$ and $\beta$ are the angles included in the spherical section, $d$ is the probe-sample separation.
FIG. 9. Experimental data and the resulting fitting for one single scan of a silver coated truncated-cone tip on a silver coated substrate. The fitted Hamaker constant is 101.46 ± 15.26 zJ.
List of Figures

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