The use of a high-pressure scanning tunneling microscope as a lithography tool for modifications of amorphous hydrogenated carbon films

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The use of a modified scanning tunneling microscope (STM) working in controlled oxygen atmospheres to create structures on the surface of a steel sample covered with 10 nm amorphous hydrogenated carbon (a -C:H) is presented. The STM lithography experiments showed the capability of producing either μm sized hills or holes depending on the oxygen pressure and the other parameters such as feedback-settings, bias-voltage, and setpoint-current. It will be shown that the hills were hollow and consisted of a locally delaminated a -C:H film induced by a dielectric breakdown between tip and sample. This explains the observed mobility and elasticity of the hills. Assuming total relaxation of the a -C:H film within the hills yielded the ratio $h/d=0.07-0.1$. The measured geometries of the hills were in good agreement with the estimated ratios. The resistance of a hill formed by the local delamination of a -C:H was measured, yielding a semiconducting behavior. The gap voltage and the total resistance decreased irreversibly, which was interpreted as a transformation of the a -C:H film within the hill to a more graphitic state. Holes were only created when all of the following conditions were fulfilled: (a) O_2 pressure greater than 1 bar, (b) low energy density dissipated in the a -C:H surface (no dielectric breakdown), (c) positive bias voltage ≥ 13 V between the sample and the tip. The Fowler-Nordheim plots $\log(I/U^2)$ vs $1/U$ for the lithography experiments that led to holes were characteristic for field emission of electrons from the tip. From this it was concluded that the process responsible for hole formation is reactive oxygen etching. Other possible processes have been excluded experimentally and theoretically, respectively. For lithography experiments performed with the feedback system on, it was possible to find lithography parameters leading to a reproducible creation of holes. © 1998 American Institute of Physics. [S0034-6748(98)02704-X]

I. INTRODUCTION

Since the development of the scanning tunneling microscope (STM) in 1985 by Rohrer and Binnig many scientists have used the STM as a tool for creating topographical structures on various kinds of surfaces. Many articles have been published in the field of nanolithography using a scanning probe microscope (SPM) as a fabrication tool.¹ The majority of STM lithography experiments focus on producing structures as small as possible. On graphite, one of the most frequently used materials for STM experiments, it is possible to create holes 4 nm in diameter and 1 nm in depth,² which is more than an order of magnitude smaller than the finest structures created by any other lithography technique. The most delicate structures were produced by Eigler and Schweizer³ in 1990, who reported the use of an STM at low temperature (4 K) to position individual xenon atoms on a single-crystal nickel surface.

Most of the published lithography experiments have either been performed in air or in controlled atmospheres of various gases at pressures between 10^{-6} mbar and atmospheric pressure. To our knowledge, none of the lithography

experiments have been made on surfaces covered with thin films.

Amorphous hydrogenated carbon (a -C:H) is an ideal coating material for use in medical applications because of its biocompatibility and outstanding tribological properties, such as its low wear rate and friction coefficient. The motivation of this work is based on the fabrication of a biocompatible sensor/actuator that can be used to measure intracellular potentials or to induce cellular responses. The construction of such a biocompatible electrode with a lateral resolution of better than 100 nm requires the ability to deposit the electrically isolating a -C:H film on a conductive material and then to modify the film.

The goal is to make holes in an a -C:H film deposited on a steel sample and then image with the same tip. Because of the high hardness⁴ of a -C:H coatings it is not possible to produce a mechanical indentation using Pt/Ir STM tips without damaging the tip. To avoid a significant change in the tip shape caused by mechanical contact, oxygen ion bombardment at room temperature will be used to locally etch the a -C:H film. This process requires the local production of

FIG. 1. Cross section of the high pressure STM system.

reactive oxygen which can be achieved by ionization and/or dissociation of molecular oxygen (O_2), by the interaction of electrons emitted from the tip. To increase the probability for this reaction to occur within the gap between the tip and the sample the oxygen pressure must be increased. Therefore the construction of a high pressure STM chamber was necessary.

The creation of hills or holes has been observed on *a*-C:H films, the type of modification depending on the lithography parameters namely the feedback settings, bias-voltage, setpoint-current, and the oxygen pressure. The possible processes responsible for the observed surface modifications will be discussed in this article.

II. CONSTRUCTION OF THE HIGH PRESSURE STM

The STM is a commercially available system, "Nanoscope III."⁵ The control software includes the capability of executing lithography commands. Figure 1 shows a cross section of the high pressure STM system used for lithography experiments. It consists of the STM scanning head built into a high pressure chamber which was designed in house. This STM chamber allows STM lithography experiments to be performed in controlled gaseous atmospheres with pressures between 10^{-2} mbar and 100 bar.

The coarse and the fine adjustment for the distance between the tip and the sample surface as well as the horizontal adjustment can be made from outside the chamber. The required torque for the fine *z* adjustment increased because of the sealing rings. Therefore, the stepping motor as well as the corresponding driver were replaced by more powerful components.

The efficiency of the local etching process is proportional to the number density of reactive oxygen species that are generated by interactions between O_2 molecules and electrons emitted from the tip. Hence the density of reactive

oxygen is determined by the emission rate of electrons, the reaction probability, and by the oxygen pressure. A high electron emission rate requires a high electric field and a high reaction probability requires an electron mean free path smaller than or at least comparable to the electrode separation. Thus the available bias voltage range of the Nanoscope was expanded from ± 10 to ± 100 V.

During preliminary lithography experiments with fixed tip to sample separation (feedback off), significant changes in the tip shape were observed due to mechanical contact with the surface. This contact always occurred at the end of the standard lithography process, when the STM system switched back to the scanning mode. This happened because the commercial control software always moves the tip toward the sample by exactly the same amount as it was retracted by the lithography command sequence (assuming that the *z* position of the surface remains unchanged during the lithography process). This software problem was solved by the insertion of additional hardware that allows the tip to be moved further away from the surface at the end of the lithography command sequence. Contact between the tip and the surface can be avoided before the feedback loop is activated again.

III. SAMPLE AND TIP PREPARATION

The *a*-C:H films were prepared by rf plasma (13.56 MHz) deposition from acetylene in a stainless-steel vacuum chamber with a base pressure better than 2×10^{-6} mbar. The films were deposited onto standard stainless-steel substrates (DIN 1.4301, AISI 304). The substrates were mechanically polished using diamond powder down to $1 \mu\text{m}$ prior to introduction into the vacuum system. The samples were mounted on the rf powered electrode and the rf generator was regulated to yield a constant self-bias. Then the substrate was Ar^+ plasma cleaned at 3.6×10^{-2} mbar and -600 V self-bias for 2 min. With the same pressure and self-bias the acetylene was introduced and simultaneously the argon was turned off so that a smooth transition from sputter cleaning to film deposition was achieved. The power dissipated in the plasma was 0.8 W/cm^2 and the growth rate of the *a*-C:H film under the conditions described above was 30 nm/min calibrated using an atomic force microscope (AFM).

The STM tips used for the lithography experiments were made of a Pt/Ir wire (80% platinum and 20% iridium). To achieve reproducible results, tips with well defined geometry must be used. For this reason all lithography experiments were performed with electrochemically etched tips. The Pt/Ir wire was dipped into a molten salt solution (10 g NaOH and 11.7g NaNO_3) at about 600°C . The current through the Pt/Ir wire into the salt solvent was measured and the etching process was stopped automatically as soon as the average current fell below a threshold value. After the etching process, the tip was cleaned in an ultrasonic bath with distilled water. As a final step, the tip was dipped into a solution of nitric and hydrochloric acid (3:1) and then held into an alcohol flame to remove the sodium on the tip. This procedure led to uniformly shaped tips with a typical radius of curvature of 300 nm (Fig. 2).

FIG. 2. SEM image of an electrochemically etched Pt/Ir tip used for lithography experiments with a radius of curvature of 300 nm.

IV. EXPERIMENTS

A. Lithography experiments

The simplest way to modify a surface using an STM is to scratch with the STM tip on the sample surface. This experiment was done with a Pt/Ir tip on a steel sample coated with 10 nm of *a*-C:H. The tip depicted in Fig. 3(a) was pushed 400 nm into the sample surface with a velocity of 1 $\mu\text{m/s}$. As shown in Fig. 3(b) the tip was blunted by this experiment. The only change of the surface, observed by imaging a 10 μm square before and after the indentation, was the apparent expansion of small structures sticking out of the surface due to the blunted tip, imaged itself by these small structures. In other words, changes on the *a*-C:H surface are not produced by a mechanical process like indentation or scratching of the tip on the surface. Therefore the observation of an undamaged tip after a lithography experiment indicates that modifications of the *a*-C:H surface produced during the experiment have to be due to a noncontact process.

Generally, noncontact STM lithography experiments can

FIG. 3. (a) The tip before it was pushed by $\Delta z = 400$ nm into the *a*-C:H surface. (b) The change of the tip shape caused by this mechanical indentation.

be done in two ways: with the separation between the sample and the tip held constant (feedback off) or with a constant tip current (feedback on). These two classes differ by the lithography parameters which can be controlled by the user. The parameters determining the modification of the surface are in both cases the same, namely, the energy flux, the potential barrier and tip-sample forces. The relationships between these parameters are clearly described by Shedd and Russel.⁶

Additionally, because the lithography experiments are performed in an O_2 atmosphere one must consider possible chemical reactions of the sample and the tip surfaces. For example, in the case of an oxygen atmosphere and an *a*-C:H sample surface one expects that chemical reactions between oxygen and the *a*-C:H surface result in an etching process.

Performing experiments with different oxygen pressures on the *a*-C:H films two different types of lithography processes were observed. Figures 4(a) and 5(a) show the corresponding Fowler–Nordheim plots $\log(I/U^2)$ vs $1/U^7$ of the measured $i(\nu)$ curves for 1 and 10 bar O_2 , respectively. During both experiments the feedback was switched off and the tip was retracted 50 nm away from the *a*-C:H surface. Then the bias voltage between the tip and the substrate was ramped from 0 to 45 V at a rate of 5 V/s (tip negative).

With 1 bar O_2 , the Fowler–Nordheim plot clearly shows field emission behavior⁸ within the bias voltage range of $25 \text{ V} < U_{\text{bias}} < 45 \text{ V}$, with currents between 50 pA and 1 nA [Fig. 4(a)]. Within this voltage range, ionized oxygen is produced between the tip and the *a*-C:H surface due to the interaction of molecular oxygen with the field-emitted electrons from the tip. The surface modification caused by this experiment was a hole etched into the *a*-C:H surface, as shown by an STM image of the modified area taken immediately after the bias voltage ramp [Fig. 4(b)]. Its depth was approximately 30 nm and its diameter 400 nm. The scanning parameters required for imaging the bottom of the hole differed significantly from the parameters suitable for the unmodified area of the sample. In particular, the scan lines over the area of the hole were noisy and the feedback system of the STM was unable to hold the setpoint current constant. We attribute this to a poorly conductive oxide layer within the hole (see Sec. IV B) caused by the oxygen etching process. As a consequence, the STM feedback system cannot react properly while within the hole and the tip shape will be slightly changed by touching the surface. Imaging the same hole with the AFM yields approximately the same geometry.

As depicted in Fig. 5(a), the Fowler–Nordheim plot for the experiment with 10 bar O_2 shows much more irregular behavior and a much steeper increase (at $U_{\text{bias}} > 36 \text{ V}$) of the current. However, for bias voltages between 31 and 36 V the Fowler–Nordheim plot can again be approximated by a straight line with nearly the same slope as in the experiment in 1 bar. This indicates that the radius of curvature of the STM tip was not changed by the mechanical contact which occurred in the 10 bar experiment during the creation of the hill.⁸ Both experiments were carried out using the same STM tip, first the 10 bar and then the 1 bar experiment. The high increase of the current in the 10 bar experiment to up to more than 1 μA (which is the saturation current of the amplifier used to measure the current) can be associated with the onset

FIG. 4. (a) The Fowler-Nordheim plot for the measured $i(\nu)$ curve. The linear behavior indicates the field emission of electrons from the tip. (b) The resulting hole in the surface due to a local etching process induced by reactive oxygen ions created by the field-emitted electrons. Lithography parameters: 1 bar O_2 , feedback off, tip to sample separation 50 nm, bias voltage ramp 0–45 V, negative tip.

of dielectric breakdown between the tip and the sample surface. This discharge leads to a highly conductive channel between the tip and the sample. Figure 5(b) shows a three-dimensional plot of the corresponding surface modification measured with the STM. The hill produced in this way had a diameter of approximately $2\ \mu\text{m}$ and a height of nearly 250 nm, which is more than the initial separation between the tip and the surface. The geometry of the hill was also measured with the AFM, yielding the same information. This implies that the tip came into contact with the growing hill and finally was immersed into the hill by approximately 200 nm (the tip having been retracted by 50 nm). The effect of the contact between the tip and the surface of the hill is still visible in Fig. 5(b). The shape of the hill, including the deformation caused by the contact with the tip, was stable for more than 1 week.

Because the positions of the polishing scratches in the sample surface relative to the scanning area did not change, one can conclude that the mechanical contact between the tip and the hill did not change the geometry of the tip significantly. This corroborates the conclusion from the Fowler-Nordheim plots that the radius of curvature of the tip was not changed by mechanical contact during the 10 bar experi-

FIG. 5. (a) The Fowler-Nordheim plot for the measured $i(\nu)$ curve. At $U_{\text{bias}} \approx 38\ \text{V}$ the current shows a very steep increase which can be associated with the onset of a dielectric breakdown. (b) The resulting hill with $h/d \approx 0.07$. This local delamination corresponds to a relaxation of the compressive stress in the $a\text{-C:H}$ film. Lithography parameters: 10 bar O_2 , feedback off, tip to sample separation 50 nm, bias voltage ramp 0–45 V, negative tip.

ment. This is surprising because in our mechanical lithography experiment where the tip was pushed into the $a\text{-C:H}$ surface a significant change in the tip geometry was observed. As will be discussed later, some of the hills are formed by the local delamination of the thin $a\text{-C:H}$ film which explains this elastic behavior.

Further lithography experiments in oxygen atmospheres with pressures greater than 1 bar showed that a large amount of energy dissipated in the $a\text{-C:H}$ film is strongly connected to the production of hills (the energy dissipated in the film is given by tip current, bias voltage, and time). However, holes were often created if the tip current stayed below a few nA, or, in other words, if the energy dissipated in the $a\text{-C:H}$ film was very small.

This relation persisted when the pressure was reduced to 10^{-2} mbar, the lowest pressure possible in our chamber. However, a much stronger electric field between the tip and the surface was necessary to create a discharge from tip to surface. At low pressures the formation of holes was not possible. Therefore it is assumed that the process responsible for the creation of holes is indeed reactive ion etching. The oxygen ions necessary for the etching process are generated by the interaction of the electrons emitted from the tip and

FIG. 6. (a) Two hills. (b) The mobility of the hills A and B. They have merged together during the creation of the hole. The dashed boxes mark the mark polishing lines in the sample to mark corresponding areas.

the O_2 molecules. When this interaction results in a dielectric breakdown hills, instead of holes, are formed.

A surprising property of the produced hills depicted in Fig. 6(a) is their mobility. Figures 6(a) and 6(b) both show the same area. The dashed boxes mark polishing lines in the sample to mark corresponding areas. In Fig. 6(a) two hills—A and B—are seen, both produced in 10 bar O_2 . In this case the hills were produced by a bias-voltage pulse ($U_{\text{bias}} = 30$ V, $T = 100$ ms) with a tip-sample distance of 30 nm. At a later stage a hole was produced just below hill B. To avoid a dielectric breakdown and thus the creation of a hill, this hole was made by scanning within a $1 \mu\text{m}^2$ scan window with a setpoint current of 150 pA (higher than the typical setpoint current of 50 pA used for imaging) and a bias voltage of 15 V in 10 bar O_2 . In Fig. 6(b) this new hole, which has the shape of a $1 \mu\text{m}$ square, is marked at the bottom of the image. Surprisingly, the creation of this hole acted as a disturbance, causing hills A and B to merge together to form hill C. After the displacement of hill B the bold marked part of a polishing scratch, which was covered by hill B in its previous position, became visible. These observations suggest that these hills are bubbles in the thin $a\text{-C:H}$ film (see Sec. IV B).

The contact resistance of hill C was investigated. For this the tip was pushed into the center of the hill by 100 nm. The original height of the hill was 200 nm. Therefore, the apex of the tip was well above the steel substrate. Furthermore, the geometry of the hill showed no permanent deformation after the tip was pulled away. This elastic behavior of the hill was significantly different from that of the untreated $a\text{-C:H}$ film after mechanical indentation and corroborates the assumption that the hill was a bubble made of the thin $a\text{-C:H}$ film.

A triangular bias voltage varying between 0 and 3 V with a time period of 2 s was applied (see inset in Fig. 7) with the tip immersed in the hill. By recording the corre-

sponding current, irreversible changes in the hill resistance were observed from period to period. Figure 7 shows the semilogarithmic plot of the resistance versus the voltage. During the first period (i) the resistance remained between $1.3 \text{ M}\Omega$ and $50 \text{ M}\Omega$. For later periods the average resistance decreased while the variation increased. The resistance characteristics of all periods show a semiconducting behavior. The resistance characteristics after period (iii) show still a semiconducting behavior but with a reduced gap.

This irreversible transformation can be interpreted as a conversion of the $a\text{-C:H}$ film from the amorphous state to a more graphitic state. Further proof will be shown that hill C actually has the shape of a bubble and hence the current must flow in the plane of the thin film. Therefore, it is reasonable to suppose that this transformation is a consequence of the high current density through the delaminated $a\text{-C:H}$ layer. As an example, the resistivity ρ_{hill} for the hill corresponding to the period (ii) at $U_{\text{bias}} = 2$ V is calculated (marked by the hollow circle in Fig. 7). Assuming a circular contact area of radius r_1 between the tip and the $a\text{-C:H}$ film and integrating over the hill radius from r_1 to the outer radius $r_2 (= 2 \mu\text{m})$ yields the total resistance, R_{hill} , which has been measured (see Fig. 7). The radius r_1 of the contact area can be estimated to 300 nm from the typical tip shape as shown in Fig. 2 and the depth by which the tip was pushed into the hill. From this ρ_{hill} can be calculated to be $\rho_{\text{hill}} = 2 \times R_{\text{hill}} \times \pi d / \log(r_2/r_1)$. With the measured resistance $R_{\text{hill}} = 500 \text{ k}\Omega$ (see Fig. 7) and the thickness $d = 10$ nm of the film one obtains $\rho_{\text{hill}} \approx 2 \times 10^{-2} \Omega \text{ m}$. Comparing this value with the resistivities of graphite ($\rho_{\text{graphite}} = 8 \times 10^{-6} \Omega \text{ m}$) and that of an $a\text{-C:H}$ film ($\rho_{a\text{-C:H}} = 2 \times 10^4 \Omega \text{ m}$),⁹ it can be seen that the resistivity of the film forming the hill is still four orders of magnitude higher than that of graphite but has become approximately six orders of magnitude lower than that of an untreated $a\text{-C:H}$ film. This is in agreement with the interpretation of the transformation of the delaminated film into a more graphitic state.

As already discussed, holes were created by lithography experiments either with the feedback system on or off. The creation of a hole as depicted in Fig. 4 was due to an experiment with a fixed tip-sample distance which enabled the investigation of the $i(\nu)$ curve containing physical information about the lithography process. Nevertheless, it was found that with the feedback system on the probability for creating holes is increased because of the controlled tip current during the lithography process. A set of lithography experiments varying the oxygen pressure has been performed with constant currents of 1 nA and fixed horizontal positions of the tip. In these experiments the bias voltages were ramped up to a certain peak voltage and held constant for 40 s (with a rising and a falling time of 1 s). As depicted in Fig. 8(b), the creation of a hole was only found at 3, 6, and 11 bar O_2 . The diameters and the depths of these holes increased with increasing pressure, as shown in Fig. 8(a). The upper and the lower limit of the pressure range for the hole creation is presumably due to the finite reaction time of the feedback system which is no longer able to suppress a dielectric discharge.

FIG. 7. Measured resistance-voltage characteristics of a hill for a triangular bias voltage (inset). (i), (ii) and (iii) represent the resistance measured at the first, fourth, and sixth upramp of bias voltage.

B. Auger investigation of modified *a*-C:H surfaces

To investigate the surfaces of the holes and hills on the *a*-C:H-coated steel sample these areas were analyzed with a scanning auger microscope (SAM). The atomic concentrations of carbon, iron, oxygen, and platinum were measured with a lateral resolution better than 1 μm . The analysis depth in the SAM is approximately 2 nm. By alternating Ar^+ sputtering with analysis, depth information of atomic concentrations within the modified regions were measured.

The untreated *a*-C:H surface consisted of 100% carbon (the existing hydrogen on the film can not be detected by the SAM). The surfaces of all the hills investigated was composed of $\geq 80\%$ carbon, 10% oxygen, and $\leq 10\%$ iron. No platinum was found on the hills.

The surface of hill C depicted in Fig. 6(b) was composed of approximately 80% carbon and 18% oxygen. The percentage of iron seen at the surface of the hill was less than 2%. After sputtering away approximately 20 nm of *a*-C:H (the sputter rate for *a*-C:H was calibrated with reference films to be 3 nm/min) the hill vanished totally even though its height before sputtering was more than 100 nm. The newly exposed surface was the steel substrate containing iron (76%), carbon (10%), and oxygen (14%). From this it is concluded that the hill was hollow and made of delaminated *a*-C:H.

The SAM investigation of the bottom of a hole etched into the sample surface by scanning a 2 μm square with the STM in 10 bar O_2 one time (with a setpoint current of 150 pA and a bias voltage of 13 V) gave the following composition: 53% carbon, 17% iron, and 30% oxygen. The high oxygen concentration within the hole supports the suspicion of a poorly conductive oxide layer mentioned in Sec. IV A. Although the depth of this hole was approximately 15 nm, which is more than the nominal thickness of the *a*-C:H layer, the bottom contained significantly more carbon than the untreated steel substrate. We attribute this to a diffusion of the carbon atoms into the steel enhanced by the locally high temperature caused by the high current density during the etching process.

FIG. 8. (a) The diameters and the depths of the created holes. (b) The pressure dependence of the peak bias voltage required for the creation of hills or holes or for leaving the *a*-C:H surface unaffected.

V. DISCUSSION

A. The origin of the hills

After the dissipation of a high amount of energy on the sample surface beneath the STM tip the formation of a hill was always observed (the typical power density can be estimated by: $\text{current} \times \text{bias-voltage} / \text{hill area} \approx 10 \mu\text{W}/\mu\text{m}^2$). This observation was independent of the O_2 pressure within the pressure range 10^{-2} mbar–20 bar. From the SAM investigation and the sputter removal of hill C depicted in Fig. 6(b), it follows that the hill is hollow and made of the thin *a*-C:H film which has locally delaminated from the steel substrate. One can conclude that the process responsible for the creation of a hill is not chemical in nature. This structure of the hill explains the observed mobility and the elastic behavior. As depicted in Fig. 6, the movement of hill B did not affect the structure of the steel substrate (see the bold marked polishing line in Fig. 6). This means that the displacement of hill B does not correspond to the horizontal displacement of material but can be compared with the propagation of a water wave. The phenomenon of forming buckling patterns in *a*-C:H films is well known.^{10,11} It is generally agreed that these patterns (sinusoidal, branching, and string-of-beads type) are formed due to a local delamination allowing a local relaxation of the compressive stress in the film. In contrast to these buckling patterns the hollow hills produced by the STM are roughly circular in shape and the compressive stress relaxation is due to the high energy density dissipated by the lithography process resulting in the local weakening of the adhesion between the substrate and the *a*-C:H layer.

The relative change in the stress ($\delta\sigma^{a-C:H}$) of the film forming a hill can be calculated by approximating the hill shape by a spherical calotte with the height h and diameter d (described in Fig. 9). With these quantities the relative change in area $\delta A^{a-C:H}$ caused by the formation of a hill can be calculated. Neglecting the shear forces caused by the conversion of the flat circle area A_{circle} into the curved calotte surface A_{calotte} , the relative change in area can be expressed by the corresponding relative change in length $\epsilon^{a-C:H}$:

$$\delta A^{a-C:H} = 2 \times \epsilon^{a-C:H} = 4 \times \left(\frac{h}{d}\right)^2. \quad (1)$$

From this it follows that the relative change in area depends only on the ratio h/d .

Applying Hook's law to an isotropic $a-C:H$ film ($\sigma_x^{a-C:H} = \sigma_y^{a-C:H} = \sigma_z^{a-C:H}$) with no stress perpendicular to the film ($\sigma_z^{a-C:H} = 0$), one obtains:

$$\epsilon^{a-C:H} = \frac{\Delta \sigma^{a-C:H}}{E^{a-C:H}} (1 - \mu^{a-C:H}), \quad (2)$$

where $\Delta \sigma^{a-C:H}$ is the absolute change in the stress, $E^{a-C:H}$ is Young's modulus, and $\mu^{a-C:H}$ is the Poisson ratio. Solving Eq. (1) for $\epsilon^{a-C:H}$ and inserting into Eq. (2), the absolute change in stress $\Delta \sigma^{a-C:H}$ can be expressed in terms of the relative change in area $\delta A^{a-C:H}$. The relative change in stress $\delta \sigma^{a-C:H}$ can therefore be written as:

$$\delta \sigma^{a-C:H} = \frac{\Delta \sigma^{a-C:H}}{\sigma^{a-C:H}} = 2 \times \left(\frac{h}{d}\right)^2 \times \frac{E^{a-C:H}}{1 - \mu^{a-C:H}} \times \frac{1}{\sigma^{a-C:H}}. \quad (3)$$

For the biaxial elastic modulus $E^{a-C:H}/(1 - \mu^{a-C:H})$ a value of 174 GPa has been measured for $a-C:H$.¹² Typically, compressive stresses of hard amorphous carbon films are in the range 2–4 GPa. Therefore, assuming complete relaxation ($\delta \sigma^{a-C:H} = 1$) of the $a-C:H$ film in the hill, h/d ratios in the range of 0.07–0.1 should be expected. The hill depicted in Fig. 4(b) possesses a ratio h/d of 0.07. This corresponds at least to the partial relaxation of the compressive stress of the film forming the hill.

B. The origin of the holes

In contrast to the hills, holes were only created when all of the following conditions were fulfilled simultaneously:

- an oxygen pressure greater than 1 bar,
- low energy density dissipated in the $a-C:H$ surface,
- positive bias voltage ≥ 3 V between the sample and the tip.

From this, it is reasonable to conclude that the process responsible for the hole formation is reactive oxygen etching of the sample surface mainly initiated by charged oxygen species generated by electron–oxygen collisions. The high electron affinity of the O_2 molecules leads to the predominant abundance of negative charged oxygen species. These reactive particles mainly impact the positively biased substrate.

The possibility that holes are produced by an indentation of the STM tip has been experimentally excluded as discussed in Sec. IV A. Another possibility to consider is field evaporation of the $a-C:H$ surface. The following estimation of the minimum required field shall exclude this possibility. The interaction energy between the electric field E and a volume with the polarization P is given by:

$$W_{P \Rightarrow E} = P \cdot E. \quad (4)$$

The polarization P of the film can be expressed by

$$P = (\epsilon^{a-C:H} - 1) \times \epsilon_0 \times E, \quad (5)$$

Calotte model for the shape of the DLC bubble:

$$A_{calotte} = A_{circle} + \Delta A; \sigma^{calotte} = \sigma^{DLC} - \Delta \sigma^{DLC}$$

FIG. 9. Sketch of the calotte model for the created hollow hills by the STM including the symbols used for the calculation of the stress relaxation.

where the $\epsilon^{a-C:H}$ is the relative and ϵ_0 is the absolute permittivity. By inserting Eq. (5) into Eq. (4) the interaction energy $W_{P \Rightarrow E}^{a-C:H}$ between a unit volume of the $a-C:H$ film and the electric field can be calculated:

$$W_{P \Rightarrow E}^{a-C:H} (\epsilon^{a-C:H} - 1) \times \epsilon_0 \times E^2. \quad (6)$$

If this interaction energy exceeds the energy needed to transform a unit volume of $a-C:H$ into atomic carbon, $W_{C-C}^{a-C:H}$, the film will evaporate due to the electric field. To estimate $W_{C-C}^{a-C:H}$, the number of C–C units having the same mass as the mass of the unit volume of $a-C:H$ ($\rho^{a-C:H}$) was calculated and equated the sum of the corresponding bonding energies (6.3 eV per C–C bond) to $W_{dissolve}^{a-C:H}$. Therefore the critical electric field $E_{crit.}$ to evaporate the $a-C:H$ surface can be expressed as:

$$E_{crit.} = \sqrt{\frac{W_{C-C}^{a-C:H}}{(\epsilon^{a-C:H} - 1) \times \epsilon_0}}. \quad (7)$$

With respect to the uncertainties of $\epsilon^{a-C:H}$, which is between 2 and 2.5,¹³ and $\rho^{a-C:H}$, which is between 2.4 and 3.1 g/cm³,¹⁴ one can calculate $E_{crit.} = 68$ –94 V/nm. This is far more than the highest field (≈ 10 V/nm) that can be applied at the lowest possible pressure of our chamber without causing a dielectric breakdown.

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