Fabrication of Nano-Tips by Carbon Contamination in a Scanning Electron Microscope for Use in Scanning Probe Microscopy and Field Emission

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Abstract. — Results are reported on a systematic study addressed to an effective fabrication of nano-tips by means of carbon contamination in a scanning electron microscope. Nano-tips with angular aperture of 10° , apical radius of about 5 nm, 1 μm long can be efficiently produced by our method in less than 60 s of electron beam exposure; it involves, in particular, successive focusing during tip growth and the use of a carbon block as a source of contaminant. These tips have been used as high aspect ratio and low capillary force probes in atomic force microscopy, and as nano-sized field emitters for electron guns.

1. Introduction

There is nowadays a wide interest in the fabrication of nano-sized tips. At least three major areas are concerned with their applications: (i) Scanning Probe Microscopy (SPM) [1], (ii) field emission [2, 3] and (iii) field emitter displays [4]. Here we deal specifically with the first two cases only; however case (iii) will benefit from progress in field (ii).

Case (i) requires *probes* with the highest possible aspect ratio (*i.e.*, the smallest tip angular aperture), mechanical strength and the smallest apical radius in order to profile irregular surfaces with steep slants and to attain high resolution. An additional requirement may be the electrical conductivity when the probes are to be used in scanning tunneling microscopy and electric force microscopy.

Case (ii) demands sharp and electrically conducting *emitters*, in order to get the highest possible current densities and coherence, with the lowest extraction voltage, for use in electron guns applied in various types of microscopy and devices.

Usually, probes are made out of metals (*e.g.*, W, Pt, Pt/Ir), semiconductors (Si) or insulators (Si_3N_4); the latter are sometimes coated with a conducting layer (*e.g.*, Au, Pd, Al) or a magnetic layer (Ni, Co) depending on the application. Emitters are made of metals or semiconductors. Here we deal with both probe and emitter tips, fabricated by carbon contamination in a Scanning Electron Microscope (SEM). Whereas this method has been pursued in several places as far as probes are concerned, nothing has been reported to our knowledge

in the case of field emitters. However, the properties of field emitters made of carbon in the form of nanotubes and diamond chips have been investigated, and the results obtained are very interesting [4–6]. This paper reports first on the deliberate enhancement of carbon contamination in an SEM, then on an optimized method for the fabrication of carbon nano-tips; examples of their applications as probes and field emitters are finally presented.

2. Carbon Contamination

Carbon contamination has been studied extensively in electron and ion microscopy with the aim to reduce and ideally eliminate it. Very little work has been done so far on the opposite problem of increasing the contamination selectively, efficiently and in a simple way; such previous work concerns the production of high aspect ratio probes at the top of cantilevers for application in scanning probe microscopy by using the electron beam of a SEM. The inconsistent results we obtained by following empirical recipes suggested by various authors (*i.e.*, use of several contaminants, such as paraffin oils or blocks), prompted us to tackle the problem afresh.

The following parameters affecting the growth of carbon contamination tips were taken into account and their effects systematically investigated.

1. SEM accelerating voltage,
2. beam current, measured with a Faraday cup,
3. beam diameter, at specimen eucentric level, and corresponding current density,
4. beam stability, focus and astigmatism,
5. specimen material, shape and clamping,
6. stub material,
7. coating before carbon-growth for non-conductive specimens.

The pressure in the specimen chamber during the investigations ranged from 5×10^{-5} to 1×10^{-4} Torr and the hydrocarbon partial pressure was about 10^{-6} Torr, measured with a mass spectrometer [7].

The assessment of the tips geometry after their growth was usually made by SEM observations with the tip placed at 90° with respect to the beam; in some cases the observations were performed in a Transmission Electron Microscope (TEM).

The results are reported below.

(i) The best accelerating voltage is 30 kV (highest value provided by our instrument, a Philips SEM 515); the beam current at the specimen level ranged from about 10^{-12} to 10^{-13} A and the corresponding *nominal* spot sizes were 20 nm and 5 nm (the emission current, read from the microscope meter, was between 100 and 200 μ A).

Since it is well known that the contamination rate C increases on decreasing the accelerating voltage V (C is proportional to $V^{-0.8}$, Fig. 1a) [8,9] and is proportional to the current density J at specimen level, one would expect the best results are obtained at low voltages. However, the gain in contamination at low voltage does not balance the contamination reduction due to the decrease of current density connected with the voltage change (Fig. 1b) [8,9]. In fact, the contamination decreases by a factor of about 2.5 by lowering the voltage from 30 to 15 kV.

Tips grown at the highest voltage show better features than those produced at low voltages, for the same values of the remaining free parameters: they have, of course, a greater height

Fig. 1. — (a) Carbon contamination C (arbitrary units) *vs.* accelerating voltage V . The trend follows the law $C \propto V^{-0.8}$. (b) Current density J *vs.* accelerating voltage V . The experimental points have been interpolated by the curve $J = 0.01V^2 - 0.15V + 1.1$. Comparison between (a) and (b) shows that by increasing V by a factor of 2 (from 15 to 30 kV) the contamination decreases by about 57%, whereas the current density increases by a factor of 5, with a net gain in contamination by a factor of 2.5.

and, in addition, a smaller cross-section at their base and a smaller apical angle, probably due to the smaller flanks of the beam cross-section than in the case of low voltage beams. An example is reported in Figure 2. It is anticipated that the use of accelerating voltages above 30 kV should be advantageous.

(ii) The smallest spot size must be used (Fig. 3).

(iii) The beam has to be well focused on the sample and well stabilised (both in position and in emission); this is obtained by running it for about 1 hour before growing the tips. The goniometer stage must be clamped, the traverse stage stable and the astigmatism carefully corrected (Fig. 4). The astigmatism correction is made at a magnification of $20.000 \div 40.000 \times$ by observing latex spheres of $1 \mu\text{m}$ diameter, coated with a thin layer of gold ($12 \div 20 \text{ nm}$). The round shape of the spheres helps in the correction. If instabilities are still present and the beam current is low, cleaning of the apertures and of the wehnelt usually improves the situation. These conditions are of paramount importance: specimen and beam drift hinder the formation of a good contamination cone.

Fig. 2. — SEM secondary electron image taken at 30 kV of two carbon tips grown on a tungsten surface showing a large difference of geometry and size. (Right side tip) Growth conditions: 15 kV, 60 s, spot size 5 nm, current density 1.1 A cm^{-2} . (Left side tip) Growth conditions: 30 kV, 60 s, spot size 5 nm, current density 5.6 A cm^{-2} .

(iv) The specimen material and shape do not seem to influence the contamination growth, at least for the types which were tested (Tungsten in the form of wires, plates and microscope filaments, Tantalum edges, Gold and Palladium films) as long as the specimen is an electrical conductor and clean. In the case of Si and Si_3N_4 cantilevers, effective C-contamination growth is obtained by first coating the substrate with a metal layer (about 20 nm thick of Au or Pd) to avoid charging up. The carbon growth is more regular on a Pd than on a Au coating film, owing to the finest size of the Pd clusters. If the above specified conditions are not well set, contamination rate is low, even with the microscope in standard order; after 10 min of irradiation only thin ($20 \div 80 \text{ nm}$) slightly bulging contamination spots of $50 \div 80 \text{ nm}$ diameter were obtained.

(v) Whether the specimen is mechanically clamped or glued with silver dag is irrelevant. On the contrary, the use of a carbon stub (with the specimen mechanically held), improves the contamination growth and the reproducibility of the results. Alternatively, simply and cheaply, use can be made of standard Al stubs to support the specimen and by placing in its vicinity a small carbon block ($\sim 50 \text{ mm}^3$). The effectiveness of the C-block depends on both its surface and its distance from the specimen region where the C-growth has to take place. The growth rate is $1 \div 2 \text{ μm}$ per minute. The adsorption properties of carbon have been known and exploited for long time. In the present situation it is believed that under vacuum the carbon block releases the contaminants previously adsorbed, thus creating a high concentration of carbon compounds in the proximity of the specimen, which favours the contamination growth [10]. The contamination effect is also well noticeable when a large C-block (surface 50 cm^2) is placed inside the specimen chamber (*e.g.*, in a corner).

Fig. 3. — SEM secondary electron image of a tip grown with a 5 nm beam diameter (left), and of the contamination spot (right) which was produced during an attempt to grow a carbon tip with a large electron beam diameter (100 nm).

(vi) Charging up effects constitute a serious problem when using high accelerating voltages, since they affect the stability of the electron beam and give rise to drift. The coating of the substrate with a metal (*e.g.*, gold) overcomes this problem. We also found that coating obtained by evaporation provides more reproducible results than sputtering.

3. Carbon-Tip Growth

The practical procedure developed to fabricate conically shaped C-tip with small full aperture angle ($< 10^\circ$) and a small apical radius (< 5 nm) is as follows.

First of all the electron beam, set at the smallest spot, is checked to be spatially and intensity stable (time required usually 1 h) and the astigmatism corrected with the help of latex spheres. The specimen on which the C-tips have to be grown is then inserted in the SEM. The electron beam is focused over an area where small details are present (observation made at $80.000 \div 160.000 \times$) near to the region where the tip has to be grown. Then the beam is stopped on the latter region. As soon as contamination is formed, astigmatism correction is again performed by observing the contamination spot. Good focusing, high stability and careful astigmatism correction are essential operations in order to achieve high quality tips; otherwise the regular shape, the sharpness and even the growth rate are jeopardised (Fig. 4).

During the growth of contamination, the Secondary Electron (SE) signal (observed in the *y*-monitor) increases because of topographic (edge) effects [11]; it increases until the tip has reached its maximum aspect ratio. The beam is then scanned and the geometrical quality of the tip assessed visually by tilting the specimen stage by 90° with respect to the electron beam.

The finest results are, however, obtained by a focusing sequence: the beam is first scanned for selecting the region of growth and for focusing, then scanning is stopped and C-growth

Fig. 4. — SEM secondary electron images of two C-tips grown under the same contamination conditions (60 s, 20 kV) except that: (right) with good astigmatism correction and good focusing; (left) after slightly altering the astigmatism correction.

initiated for a short time (≈ 20 s); after that, scanning is resumed (thus the contamination process is drastically reduced), the magnification is increased for refocusing and then the C-growth is re-started by stopping the scanning again, and so on for 2 or three times. In other words the top of the initial C-cone is used as the starting point for the following contamination instalment (Fig. 5).

The results of the application of the two methods (just one focusing and several focusing procedures) show two different types of tip geometry. In the first case, the tip shape is that of a paraboloid rotationally symmetric; in the second case, the tip shape is that of a superposition of frustocones which end with a paraboloid (Fig. 5). Details of the tips fabricated with single and multi-focalisations have been obtained from high resolution images (~ 0.3 nm) and examples are presented in Table I (see also Fig. 6a).

A particular case of growth is shown in Figure 6b, where a protuberance of radius ≈ 1 nm has been formed at the end of the tip, probably due to a small shift at the very end of the growth. We intend to investigate this fact which may lead to the formation of tip ends smaller than the beam dimension.

Nano-diffraction and high resolution imaging have demonstrated that the tips are formed by amorphous carbon.

The tilting stage may also be used to grow tips with their axis inclined with respect to the substrate surface normal (up to $\pm 60^\circ$), as in the case of Si_3N_4 cantilevers (Fig. 7). This possibility may be relevant in profiling problems (see Sect. 4.1).

Fig. 5. — FEG/TEM images of two carbon tips grown in a SEM under the same conditions except for refocusing. (left) The regular shape of the tip (practically a frustocone ending with a hemisphere) indicates a single initial focalisation. (right) The irregular shape, formed by overlapping truncated cones, is the result of successive refocusing. The points where focusing has taken place correspond to the steps and changes in slope. Marker = 100 nm.

Table I. — *Geometrical carbon-tip parameters according to the focusing method used during growth.*

Type of growth	Tip height nm	Tip base diameter nm	Width at half height nm	Full angle degrees	Apical radius nm	Growth time s
Single focalization	500 ÷ 600	100 ÷ 130	60 ÷ 80	8 ÷ 10	10 ÷ 16	20 ÷ 60
Successive focalizations	600 ÷ 1500	50 ÷ 90	30 ÷ 60	4 ÷ 8	2 ÷ 6	20 ÷ 60

a)

b)

Fig. 6. — (a) TEM/FEG high resolution image of a tip apex. The tip seems to be formed by amorphous carbon; this result has been confirmed by nanodiffraction. (b) TEM high resolution image of a tip apex ending with a small protuberance of radius about 1 nm. The markers represent 10 nm in both images.

Fig. 7. — SEM secondary electron image of a nanoprobe fabricated by carbon contamination at the top of an AFM Si_3N_4 pyramidal tip. Note that the nano-tip has been deliberately grown inclined by 10° with respect to the pyramid axis, in order to perform scanings perpendicularly to the specimen surface.

4. Applications

Two applications are presented: (i) the case of topographic improvement and, (ii) the case of field emission.

4.1. Topography

The same specimen of known structure has been sequentially observed in an AFM with two different cantilever tips, but otherwise under the same experimental conditions. The specimen is a cross-grating of square pits (holes) having a size of 500 ± 15 nm and a depth of 193.6 ± 6.3 nm (as specified by the supplier); their spacing is $1 \mu\text{m}$.

It was first observed in the contact mode by using conventional Si_3N_4 type of cantilevers with a pyramidal tip (apex angle 68°) in Digital Instrument, Multimode III and then with similar types of cantilevers where at the top of the Si_3N_4 pyramid a carbon nano-tip had been grown with the method described in Section 3 (Fig. 7). The growth angle was 10° with respect to the pyramid axis, so that the scanning of the specimen was performed with the C-tip axis perpendicular to the sample surface.

From Figures 8a and b, it is apparent the superior quality and accuracy of the image obtained with the carbon nano-tip, in particular with respect to the shape and size of the holes, and to the possibility of probing their bottoms. On the contrary, the images produced by the use of conventional tips clearly show the convolution of the hole with the tip shape: the (false) taper angle of the hole is the same as that of the pyramidal tip angle. Quantitative results worked out by observing a series of holes are reported in Tables II and III. Within the experimental and statistical errors, the dimensions of the holes are consistent with those supplied by the manufacturer of the grating, confirming that practically no artefacts have been produced by the nano-tips. The hole sizes reported in Table III have been measured at the top of the profile.

Table II. — *Hole depth.*

Hole	Standard Si ₃ N ₄ pyramidal probe Hole depth (nm)	C-nanotip Hole depth (nm)
1	164	201
2	165	199
3	158	201
4	157	200
5	159	194
6	160	197
7	164	193
8	168	194
9	162	196
10	162	193
Average depth and statistical error (3σ)	169 ± 9	197 ± 9
Manufacturer's data	193.6 ± 6.3	

Table III. — *Hole size.*

Hole	Standard Si ₃ N ₄ pyramidal probe Hole size (nm)	C-nanotip Hole size (nm)
1	429	503
2	429	488
3	424	490
4	434	487
5	427	479
6	428	505
7	433	488
8	429	489
9	435	488
10	426	490
Average size and statistical error (3σ)	429 ± 10	491 ± 22
Manufacturer's data	500 ± 15

Fig. 8. — Cross-grating calibration standard with blind holes (pits). AFM topographic images acquired in the contact mode and corresponding sections (y -modulated) along the vertical continuous line. (a) The probe is a standard Si_3N_4 pyramidal tip. (b) The probe is a carbon nano-tip grown at the apex of a Si_3N_4 pyramid. To be noted both the shape and symmetry of the profile, the latter being due to the C-tip scanning the sample perpendicularly to its surface.

Carbon nano-tips offer two great advantages compared to standard tips: (i) they reduce (and in some cases render negligible) the artefacts connected with the tip shape (without recourse to complex deconvolution procedures which require the knowledge of the tip shape and size) in all those cases where the specimen surface contains steep slants and, (ii) the adhesion forces between the tip and the sample are reduced by a factor of about 10, as can be seen in Figure 9; this advantage, of paramount importance in the observation of soft organic and biological samples, results from the small apical size of the C-tips and possibly from the water/carbon interaction. It has been noted that the C-tips are brittle and tend to chip off in the presence of lateral forces (Fig. 10), whereas the standard tips are much more robust.

4.2. Field Emission with C-Tip

Tips fabricated with the method described in Section 3 have been grown at the apex of electron microscope tungsten filaments and tested for emission in a ultra-high vacuum system (pressure less than 5×10^{-9} Torr). Field emission takes place, and currents from a few pA up to $0.2 \mu\text{A}$

Fig. 9. — Force-distance curves obtained with the same cantilever, showing the different capillary forces acting on a calibration standard: (a) in the case of a conventional Si_3N_4 pyramidal tip and (b) in the case of a carbon nano-tip grown on it.

have been measured on changing the extraction voltage. Figure 11 shows a typical result obtained. The change of slope during this run is attributed to a change in the emission area, possibly due to contamination or rearrangement of the tip atoms.

We are currently investigating the possibility of improving the emission stability.

5. Conclusions

An optimised method has been presented for growing amorphous carbon tips by carbon contamination inside a scanning electron microscope. The method is simple, effective, reliable, versatile, controllable and cheap. It is performed on a conductive surface, at an accelerating voltage of 30 kV; however, the use of higher voltages, if available, will be advantageous. The main features of the method are: use of a carbon stub (or a carbon block) as a source of

Fig. 10. — SEM secondary electron image of latex spheres deposited on a gold-coated graphite surface after several observations in an AFM. To be noted the two broken tips lying near the large sphere. The marker represents 1 μm .

contaminant, and controlled focusing and astigmatism correction during the tip growth. The results can be immediately assessed.

Probes can be prepared with this technique in about 60 s; they have a conical shape with the full angle as small as 10° and the length of 1 μm . However, the height can be varied within a large range (from less than 1 μm to several tens of μm) by varying the contamination time. An example of application in the imaging and measurement of depth and size of blind holes has been given and comparison has been made to the case of using standard tips. It has also been shown that the capillary forces acting on a carbon nano-tip are smaller by one order of magnitude with respect to those acting on standard tips under the same conditions.

Nano-tips made by carbon contamination (radius less than 5 nm) have been grown at the apex of ordinary electron microscope tungsten filaments, and field emission has been demonstrated to take place; its features are similar to those obtained with pointed tungsten filaments under the same geometrical conditions. However, current instabilities are a problem, which are believed to be related to the pressure in the field emission chamber, around 5×10^{-9} Torr. Modifications to the chamber to improve the vacuum are in progress.

We envisage the exploitation of such arrangements in electron microscopes equipped with field emission guns. The use of standard pointed-filament (with their own sockets) at the top of which carbon nano-tips are grown under controlled conditions in a scanning electron microscope will allow their re-utilization in TEM/FEGs or in STEMs without the need to change neither the configuration of the gun electrodes, nor the related electronics, as might be required for re-sharpening blunt tungsten tips for field emission guns [12]. Carbon tips grown on an electrically conducting substrate may also be used in scanning tunneling microscopy.

Fig. 11. — Experimental Fowler-Nordheim plot obtained from a carbon-contamination grown nano-tip used as field emitter at a pressure of less than 5×10^{-9} Torr. At 2600 V the emission current is 2.6 nA. The two trends are attributed to emission changes due to contaminants or geometrical changes.

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