# Deposition of nanoscale rhodium dots by STM assisted CVD

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**Abstract** : Direct patterning of nanometric metallic features is possible by local decomposition of gaseous molecules on a surface, induced by application of a pulse voltage on a STM tip while surface imaging. Decomposition reaction occurs above a threshold voltage of 2.7 V corresponding to an electric field of about 5.4 $10^7$ V.cm$^{-1}$ between STM tip and sample. Metallic Rhodium dots as small as 3 nm can be deposited using this method. The kinetics of formation of these dots are discussed and a reaction mechanism is proposed.

## 1. INTRODUCTION

The high resolution reached with proximal probe microscopes -i.e. Scanning Tunneling Microscope (STM), Atomic Force Microscope (AFM) and Scanning Near field Optical Microscope (SNOM) -, makes these microscopes suitable for lithography application to reach nanometric resolution required for Single Electron Device elaboration. The resolution gain has been demonstrated and nanoscale devices have been elaborated with these techniques. Except results based on the mechanical interaction between an AFM tip and a soft substrate (mechanical indentation of polymer resists [1, 2] or self assembled monolayers [3]), most of these lithography techniques take advantage of the spatial resolution of the electronic emission from the microscope tip to perform local physical or chemical alterations on a suitably prepared surface. Following this principle, a wide range of different techniques were investigated among which the Chemical Vapor Deposition (CVD) under the tip of a STM [4, 5] seems to be a very promising technique to build nanostructures.

Chemical Vapor Deposition assisted by STM (STM assisted CVD) is a very interesting field of study since the growth mechanisms involved in the reaction are peculiar to this technique. For example in the case of heavy molecules, the reaction volume involved is so small (few nm$^3$) that under low pressure ($10^{-3}$ mbar) only one molecule enter this volume per millisecond. Consequently this technique offers the possibility of molecule by molecule deposition with a precise positioning.

Direct patterning of nano-dots of rhodium on gold surface has been achieved by STM assisted CVD by decomposition of the inorganic precursor $[Rh(PF_3)_2Cl]_2$ induced by application of pulse voltages on a STM tip. The influence of pulse polarity has been studied. The reaction kinetics at room temperature have been investigated. To understand the growth mechanism, the influence of gas pressure and pulse duration has been studied.

## 2. EXPERIMENTAL SET-UP AND PROCEDURE

The experimental set-up is presented figure 1. Briefly, the STM is placed inside a stainless steel chemical chamber. The base pressure of $5.10^{-7}$mbar can be reached in few hours by pumping with a turbomolecular pump, without baking the chamber. The chamber is fixed on a bulk steel plate insulated from low frequency vibrations by shock springs.

In order to perform electrical tests on the nanodevices elaborated, these devices have to be linked to micronscale command electrodes previously drawn on the substrate surface. Due to the weak scan window of commonly marketed STM (about 8 µm), the STM tip has to be engaged on the substrate surface inside this test pattern with a precision better than 4 µm. Consequently, an optical microscope coupled to a video camera has been fitted to the chamber and allows the observation of the substrate during the tip engagement step.

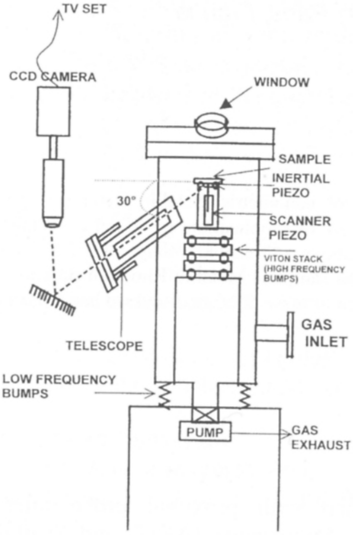

Figure 1 : experimental set-up

The precursor is the inorganic molecule $[(PF_3)_2RhCl]_2$. It is elaborated by the procedure described in literature [6] adapted to a small compound quantity (typically 0.2 g of chloro (1, 5-hexadiene) rhodium dimer reacted with $PF_3$ in pentane. The precursor was purified twice by sublimation leading to large red crystals that are easily handle and not too air-sensitive. The molecule characteristics have been presented in previous papers [7 , 8].

Experiments are performed in a static atmosphere of pure precursor. The gas pressure was varied in the range of $10^{-4}$ to $10^{-2}$ mbar.

Deposition is performed on gold coated mica substrates. The gold layer is elaborated by evaporation under vacuum at high temperature (400°C). These leads to atomically flat gold surfaces on areas as large as about 100 x 100 $nm^2$, so flat enough to easily image the surface by STM and wide enough to perform local CVD at nanometric scale. Figure 2 shows a typical as deposited gold surface.

During STM experiments, a bias is applied to the sample and a feedback loop maintains the tunnel current flow between the tip and the sample at a given setpoint value (typically 0.1 to 1 nA) while the tip is scanning the surface. Surface is imaged under typically 100 mV substrate bias and at a current setpoint of 300 pA. In these conditions, the tip surface distance is about 0.5 nm [9].

Lithography is performed by application of a pulse voltage on the substrate surface at a given position on the substrate leading to local decomposition of the molecules. In fact, according to the small tip-sample gap (about 0.5 nm) a pulse voltage of 3 V leads to a high electrical field of $6.10^7$ V/cm allowing the decomposition of the molecule. In order to avoid tip surface contact while rhodium dot is growing, the feedback loop of the STM is maintained during pulse voltage application. Besides, since the current flow is fixed at the required setpoint value during deposition, tip removal while the voltage pulse is applied to the sample is avoided providing the pulse duration has been chosen lower than the reaction time of the feedback loop of the STM (about 200 µs). Consequently, the electric field is constant during pulse application.

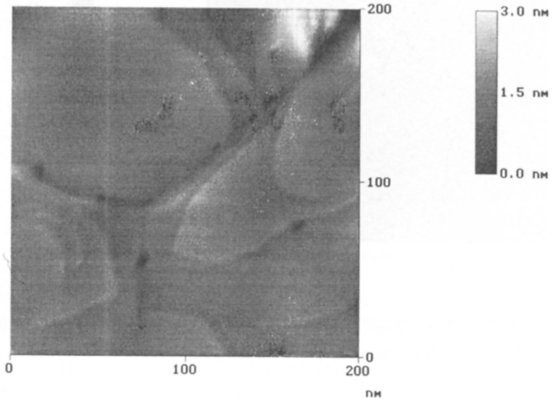

Figure 2 : gold coated mica surface as processed observed by STM.

Tips are prepared by electrochemical etching of a platinum wire. This technique allows to obtain very sharp STM tips (curvature radius of about 5 nm) [10] avoiding multiple tip effects.

The kinetics of rhodium dot deposition on gold surface have been studied as a function of gas pressure and pulse duration.

## 3. RESULTS AND DISCUSSION

### 3.1 Pulse polarity influence

Deposition of rhodium was only observed when negative pulses were applied to the sample in presence of gas precursor, above a threshold of –2.7 V. Note that in the same experimental conditions, no reaction is observed without precursor in the chemical chamber and consequently, the deposited atoms come from the precursor decomposition and not from an atom transfer from tip to sample. According to its symmetry [7], the precursor molecule $[Rh(PF_3)_2Cl]_2$ does not present a polarisability behaviour. Consequently, it seems that since the pulse polarity plays a role in the deposition process, the molecule is probably dissociated in several radicals during pulse application. One of these radicals has a positive charge and is attracted by the negatively biased surface.

### 3.2 Dot dimensions and characterization

Figure 3 shows a series of rhodium dots deposited under a gas pressure of $5.10^{-3}$ mbar and after application of 200 voltage pulses of 200 µs at a frequency of 200 Hz. The typical diameter of these dots is 3 nm and the dots are separated by 4 nm apart. This resolution limit has been already reported [11]. Note that this patterning resolution fits with lithography requirements for Single Electron Device elaboration.

No conventional characterization can be performed on such small structures and consequently, the actual composition of the dots is not defined. However the STM equipment allows to obtain simultaneously a topographic and a current contrast image of the surface. In this latter case the image contrast consists in the local current error between the actual local tip-sample current and the current setpoint chosen for the feedback loop control. The current image clearly showed that when the STM tip arrives above a deposited cluster while surface scanning, the current error increases which means that the local current measured on the dots is higher than on the substrate surface. Consequently the dots have a rather metallic behaviour.

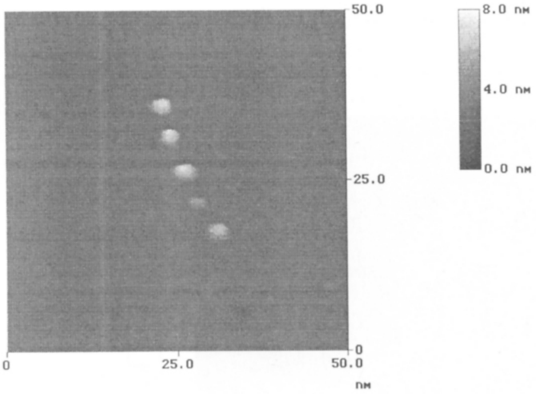

Figure 3 : series of rhodium dots performed by application of 200 voltage pulses. The pulse voltage was –2.8 V and the pulse duration 200 μs.

### 3.3 Electric field effect or current effect

A particular attention has been paid to tip preparation. Tips are elaborated from a 150 μm diameter platinum wire. It is well known that tips obtained by knife cutting are suitable for imaging application of STM. In fact, since the tunnel current flow depends exponentially with the tip-sample distance (the current decreases of one order of magnitude when the tip is removed of 0.1 nm from the surface [9]), tunnel effect is only observed between the external atoms of the tip and the substrate surface. Consequently if a double tip is obtained during wire cutting, it will have no effect on the image result. However, it has been observed that a double tip leads to the formation of a double dot on the surface during pulse voltage application. Assuming that molecule decomposition is due to the current flow between tip and sample, a double tip should not affect the decomposition process since the current flow between the surface and both parts of the tips are not of the same order of magnitude.

In fact, contrarily to the current flow, the electric field between both parts of the tip and the sample are nearly the same, which induces the formation of two separated dots. Finally, the decomposition process is due to an electric field effect rather than a current flow effect.

### 3.4 Reaction kinetics

The volume of rhodium dots deposited has been studied as a function of gas pressure (figure 4) at a fixed pulse voltage of –2.8 V. For each experiments the dot volume has been measured by STM imaging after application of 200 pulses, 200 μs wide at a frequency of 200 Hz (i.e. for a cumulative time exposure to electric field of 40 ms). The volume deposited is proportional to the gas pressure. Note that in these conditions, no deposition was observed below a pressure of $10^{-3}$ mbar. Let us call this value a pressure threshold.

The linear relationship between deposited volume (and consequently the deposition rate) and the gas pressure suggests that the reaction is mass transport limited. The reaction can occur in the adsorbed layer or in the gas phase.

The molecule flux per unit time and surface is given by the kinetics theory of gases:

$$\Phi\ (m^{-2}.s^{-1}) = \frac{P}{(2\,\pi\, m\, k_B\, T)^{1/2}} \qquad (1)$$

where P, m and T are the gas pressure, molecule mass and gas temperature respectively.

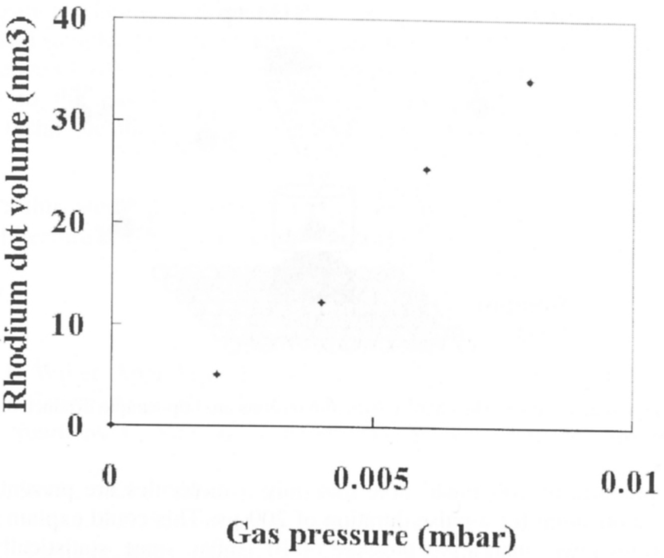

Figure 4 : influence of gas pressure on the volume of rhodium dots obtained after application of 200 pulses. The pulse voltage was -2.8 V and the pulse duration 200 µs.

However, due to the tightness of the tip-sample distance (0.5 nm) regarding to the curvature radius of the STM tip (5 nm), the tip presence immediately above the surface induces a screening effect of the molecule flux on the surface just at the level of the tip apex. In fact, no molecule can reach this particular surface point from the solid angle containing the STM tip. Numerical application allows to estimate that this shadowing effect decreases by a factor 2 the molecule flux given by equation (1). Finally, under a gas pressure of $5.10^{-3}$ mbar, a flux $\Phi = 1500$ molecule.nm$^{-2}$.s$^{-1}$ is found.

Figure 5 presents the geometry of the tip-sample system. A cylindrical characteristic volume can be defined within tip-sample gap and corresponding to the space area in which a molecule can be decomposed by the tip. The local electric field on the substrate surface at a distance R from the projection of the tip apex on the substrate is given by the following equation [12] :

$$E(R) = \frac{a(a+b)(2b+a)}{2b[(a+b)^2+R^2]^{3/2}} V$$

where $V$ is the voltage applied to the sample, $a$ the curvature radius of the STM tip (typically 5 nm) and $b$ is the tip-sample distance (about 0.5 nm). Thus the height of the cylindrical characteristic volume is the parameter $b$ and the diameter of this cylinder can be defined as the full width at half height of the E(R) curve (i.e. 8 nm). Finally the total surface of the characteristic volume is about 60 nm$^2$.

Consequently the molecule flux in this characteristic volume is $90.10^3$ molecules.s$^{-1}$ for a gas pressure of $5.10^{-3}$ mbar. The effect of gas pressure has been studied at a fixed cumulative time of 40 ms, which means that about 3600 molecules entered inside the characteristic volume during pulse application. At this gas pressure, the dot volume was found to be 19 nm$^3$ (figure 4), which corresponds to a cluster containing 1420 rhodium atoms. Consequently, the reaction is mass transport limited with a reaction yield in the characteristic volume of about 40 %. Note that the molecules are probably decomposed only at the centre of the characteristic volume where the electric field is maximum and the reaction yield might approach unity.

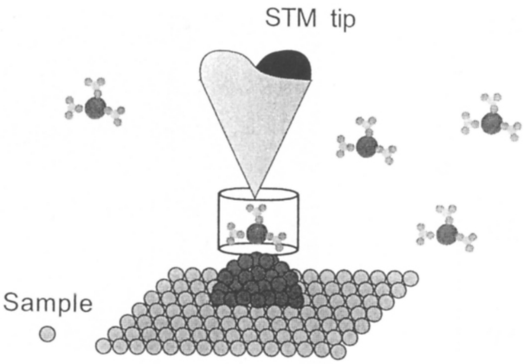

Figure 5 : tip-sample system modellization. The characteristic dimensions are : tip-sample distance 0.5 nm and diameter at half height of the E(R) curve 8 nm.

Under a gas pressure of $10^{-3}$ mbar, note that only 3 molecules are present in the characteristic volume during pulse application for a pulse duration of 200 µs. This could explain why no deposition is observed under pressures lower than a gas pressure of $10^{-3}$ mbar, since, statistically, only one molecule would be present in the reaction volume during one pulse. However a much greater number of pulses might lead to deposition of rhodium atoms on the surface.

It has been observed that for pulse duration of 50 µs, the pressure must be higher than $5.10^{-3}$ mbar to obtain a deposit, after application of 200 voltage pulses. The pressure 'threshold' is proportional to the reciprocal pulse duration.

The reaction is mass transport limited but the reaction occurs either in the gas phase or in the adsorbed layer, depleted by molecule consumption during pulse application under low gas pressure. The pulse frequency was fixed at 200 Hz that means that the time between two successive pulses (5 ms) is longer than pulse duration investigated (50-200 µs). Under a gas pressure of $10^{-3}$ mbar, and for pulse duration of 200 µs, it has been shown that only three molecule passes through the characteristic volume during pulse application and only one molecule is dissociated by the pulse. Assuming a step of molecule adsorption in the growth mechanisms, deposition might be observed for pulse duration of 200 µs and at a gas pressure of $10^{-3}$ mbar (pressure threshold for this pulse duration) since between two successive pulses (5 ms) the adsorbed layer can be entirely renewed. In fact between two pulses 90 molecules are impinging on the surface.

Consequently the reaction is mass transport limited and occurs in the gas phase and the molecules are dissociated when passing between STM tip and sample during pulse application to the sample.

## 4. CONCLUSION

Lithography at nanometric scale is possible by direct patterning of metallic features using the STM assisted CVD technique. The gaseous molecules are decomposed within the STM tip-sample gap by triggering a series of high voltage pulses on the sample when the tip is positioned on the surface at the desired location.

Metallic Rhodium dots nanostructures have been drawn by decomposition of $[Rh(PF_3)_2Cl]_2$ molecules. Rhodium dots are observed only when negative pulse voltages are applied to the sample. Rhodium clusters as small as 3 nm can be easily obtained by this technique.

The decomposition reaction occurs in the gas phase and molecules are simply dissociated when passing between tip and sample, space in which the electric field is very high (about $3.10^7$ V.cm$^{-1}$). Under gas pressure in the range of $10^{-3}$ to $5.10^{-3}$ mbar, the reaction is mass transport limited and the deposition rate is proportional to the gas pressure. A reaction yield of 40% is obtained for the precursor decomposition. This technique allows to control a CVD reaction molecule by molecule.

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