Chapter 8

Summary and conclusions

"Or eccomi giunto al nord cap. Che e dire all'extremita di fiunmarka anzi. Pero co'terminata la mia curiosita."
Francesco Negri, 1664

Electron Beam Induced Nanometer Scale Deposition

Miniaturization, micromachining and integration started as a trend in electronics manufacture in the mid-seventies and is still continuing at this moment, extending rapidly to other fields like molecular biology, analytical chemistry and mechanical engineering. Twenty five years ago the resolution requirement for integrated circuits was 10 μm while today it is approaching 100 nm. Structures with sizes between 100-500 nm are fabricated on industrial scale, at throughputs of many wafers per hour, offering fascinating applications. The challenge of large scale manufacturing for the immediate future is to find the right methods to fabricate sub-100 nm features. The promising candidates for the so-called nanolithography are: the extreme ultraviolet lithography, ion and electron projection systems and X-ray proximity printing.

In the research laboratories, another community is exploring the future of nanotechnology. Here the so-called laboratory nanofabrication methods are theoretically investigated or experimented. The main purpose of laboratory activities is to demonstrate that, as R. Feynman would say, "little has been done, but an enormous amount can be done in principle" [1]. At this moment in research laboratories, features between 10 and 100 nm can be fabricated on a day to day basis using electron beam lithography (resist based or electron beam induced deposition (EBID)) at throughputs of ca. 25 - 250 Mpixels per second. The need to control and manipulate things on molecular scale drives the search for methods to fabricate sub-10 nm structures. In scanning probe lithography (STM or AFM) 1 nm features can be fabricated using EBID with a speed of a few Mpixels per second and 0.3 nm size structures can be arranged by atom manipulation, with a speed of ca. 1 atom per minute. However the scanning probe procedures are extremely slow, unacceptable for an industrial process, and even for many research purposes.

Promising alternatives to scanning probe atomic manipulation are the focused energetic beams (photon, ion and electron). Among these techniques, electron beam lithography offers the best resolution. The problem is that the electron beam lithography using a conventional resist (PMMA) has reached its fundamental resolution limits, imposed mainly by the electron scattering in the resist and the resist grain size. This limit is set at 10 nm and this barrier turned out to be very difficult to break with any other nanofabrication method.

In this context, we investigate the potential of EBID to fabricate sub-10 nm features. EBID is a resistless, direct writing technique which might suffer less from the proximity effects that gave headaches to PMMA lithography. The driving force is the fact that nowadays electron optical systems with 0.2 nm beam diameter are available. EBID performed in such a Scanning Transmission Electron Microscope (STEM) might be a potential sub-10 nm fabrication technique. This is a less conventional manner to approach nanofabrication with electron beams, because STEM is only known as a commercial tool for high resolution material analysis. STEM offers an environment very favorable for high resolution EBID: a thin substrate, a very fine and stable focused beam (0.2 nm is the state-of-the-art), good control of the beam focus and positioning. This thesis contains the theoretical and practical demonstration of the viability of this idea.

An extensive literature review on electron and ion beam induced deposition has been performed. The results show that in principle EBID can deposit continuous and sufficiently conductive metal lines, both on bulk and thin specimens. The intriguing fact was that even with a 2 nm diameter beam, the smallest structures deposited elsewhere were 13 to 20 nm. A theoretical model that could explain this lateral broadening did not exist at that moment. It is our main goal to estimate the size of structures fabricated with EBID for given beam, target and precursor parameters.

The theoretical estimate of EBID fabrication resolution is a long and complicated procedure. Things would have been easier if only the primary beam would be the main player in EBID. Then structures as wide as the probe size could be fabricated and the use of modern electron microscopes with 0.2-0.5 nm diameter probes would easily fabricate sub 10 nm structures. Unfortunately, a simple experiment shows that even such a fine beam grows on a thin target tips with diameters of 20-30 nm. This is a trivial demonstration that also other factors are playing a role in deposition, some of them influencing its resolution. The problem has been solved using a straightforward strategy: factors that might play a role in lateral evolution of deposited structures are identified and their contribution quantified as accurately as possible.

The secondary electrons (SE) emitted as a result of primary bombardment are the most suspected factor, due to their low energy range overlapping with the dissociation cross section peak for most of gaseous precursors. We developed a procedure to predict the shape of a singular dot grown by EBID in an electron microscope as determined by the secondary electrons.

For this purpose a Monte Carlo simulation program for the electron scattering in a flat solid target has been written. The user friendly interface can be also useful for student presentations, because the process parameters can be changed easily and the electron trajectories are graphically displayed. The results of MC simulations show where the SE emerge and what energies they have. The difference with other MC simulations is that we coupled these results with the electrons power to dissociate molecules. Their contribution to deposition depends on their energy and on the sensitivity of the gas molecule, characterized by the molecular dissociation cross section of the gas molecule, $\sigma_{diss}(E)$. After reading a lot about electron - gas interactions we discovered that this property is very unknown. Even the most simple molecule, hydrogen H_2 creates enough problems to the chemists, and in 2001 still new empirical formulas are issued for its electron impact induced dissociation. The problem is that a large number of possible dissociation paths exists, and this number grows with the complexity of the molecule. EBID unfortunately uses precursor gas molecules with a complicated structure, making this task not trivial.

The results of our simulations show that the SE emerging on the flat surface of the thin target create a dot clustered in an area of 2 nm around the primary beam axis. This is the ultimate limit in EBID, determined by SE.

The question is why in reality a stationary 0.2 nm electron beam still deposits 20 nm diameter dots? Our discovery is that later in time, the SE emitted from the flanks are laterally broadening the tips until a saturation value is reached. The dots shape tracing is necessary also after a structure begins to grow and this is performed by extending the MC for flat surfaces with a profile simulator based on cellular automata. The saturation value is the routinely obtained resolution and agrees with the values reported by many authors. The problem is that structures as narrow as 1 nm can be fabricated, but they will be very thin. Very soon the diameter will expand, so the exposure has to be very low.

The results of this exercise was that we understood the role of SE in deposition and know how to make smaller structures.

Other influences have been also estimated. The delocalization of inelastic scattering happens because an electron can lose energy also at a distance away from its inelastic scattering center. The necessity to study this effect has been suggested by a few authors, but no quantification has been made yet. Only a range is usually given as between 0.1 and 10 nm. It is a difficult problem. We calculated the spatial extent of delocalization of SE. Our results show that the delocalization of SE generation can broaden the SE profile with about 0.1 nm. Other influences, like migration of fragments and electric field effects, have been also investigated.

The first experimental system where we studied EBID is the dual beam instrument, based on a Philips EM 420 STEM and a home made ion column. This system is designed as a workstation in an ambitious project started at Delft University of Technology in cooperation with the FOM foundation, the NEXT laboratory.

The electron beam column has been made operational and additional elements necessary to host EBID have been added. The computer controlled pattern generator and two possible variants for a gas delivery system are described. A nozzle injector gas delivery system has been designed for the Philips EM 420 STEM. It can be used for both electron and ion induced chemistry. EBID has been tested in this system with the conclusion that electrostatic deflectors also work for the positioning of the electron beam and the $W(CO)_6$ precursor operated at room temperature creates enough gas flow to obtain deposition. The limitations of the system were the spot size and the probe current.

In order to perform EBID experiments in another higher resolution STEM, a portable environmental gas cell, that can be used without modifications to the microscope has been designed.

Encouraged by the theoretical estimations that pointed out that sub 10 nm lithography is possible using EBID, we dedicated the last chapter to high resolution experiments. Successful high resolution experiments with contamination in a state-of-the-art STEM have been obtained. Continuous contamination lines with FWHM ranging from 3 to 8 nm have been deposited. Also very thin and narrow lines with FWHM of 1.3 nm could be obtained. Difficulties have been encountered in their visualization because the thickness is less than 10 nm. Other imaging methods as AFM should be tried.

This thesis is organized as follows:

- an extensive literature review on EBID and IBID

- the know-how on Monte Carlo techniques used for simulation of secondary electron emission from a target bombarded by electrons and a computer program to demonstrate their use for EBID profile simulation.

- a literature search on gas-electron interactions and properties of precursors used in contamination lithography and EBID.

- a theoretical model that demonstrates the role of SE in EBID spatial resolution.

- an evaluation of the influence of the delocalization of electron inelastic scattering on EBID

resolution.

- the design of additional elements necessary for the EBID and IBID experimental study in a STEM: a computer controlled pattern generator, imaging facilities and two gas delivery systems (nozzle injector and a gas environmental cell)

- experiments on high resolution line deposition that show that sub 2 nm is possible.

In conclusion we could give a reasonable answer to the questions formulated in the introduction in Chapter 1. We demonstrated theoretically and experimentally that EBID can be used in a STEM and if this STEM is a very high resolution one, it can host sub 10 nm deposition.

We now know that structures smaller than reported before can be obtained with EBID.

We know that the previously observed lateral broadening of the structures is not due to the secondary electrons emitted from the flat substrates. The broadening is caused by the secondary electrons generated in the freshly deposited structure. This effect has been beautifully demonstrated by Monte Carlo simulations.

The shapes of experimentally obtained dots are in agreement with the results of Monte Carlo profile simulations.

In the future efforts have to be made to prevent EBID to remain just a laboratory nanofabrication technique. To be promoted among other nanotechnology methods, an EBID system has to be built that fulfills the strict industrial lithography standards, as patterning at high speed, patterning with low distortion, high linewidth control, reproducibility and high overlay accuracy.

Bibliography

[1] R.P.Feynmann. There's plenty of room at the bottom. *APS meeting, California Institute of Technology* (1959).