In-situ Monitoring of Gas-Assisted Focused Ion Beam and Focused Electron Beam Induced Processing

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Abstract. The state of the art of several in-situ monitoring techniques for gas assisted focused ion beam and focused electron beam induced processing (FIBIP and FEBIP) is presented. The monitoring techniques discussed comprise (a) the stage current and secondary electron signal for topographic information, (b) mass sensors to determine process yields, deposit density, molecule coverage and adsorption, (c) electrical resistance measurements, (d) reflectometry, (e) annular dark field sensing, and (f) SEM integrated mechanical measurements.

1. Introduction
Focused electron beam (FEB) and focused ion beam (FIB) induced processing are well established techniques for local deposition and etching that rely on decomposition of surface adsorbed precursor molecules by irradiation, see fig. 1.

Fig. 1: Principle of gas assisted FEB or FIB processing (for sake of clarity the FIB sputtering mechanism - proceeding without gas assistance – was omitted). Volatile molecules are introduced into the microscope chamber and reversibly physisorb on the substrate surface. Dissociation of molecules is taking place by charged particle (electrons or ions) irradiation: a) Deposition: the dissociation reaction results in non-volatile fragments forming the functional deposit, b) Etching: the dissociation products form volatile compounds with the substrate and remove material from the bulk.
These high-resolution nanostructuring techniques have various applications in nanoscience and industry comprising attach-and-release procedures in nanomanipulation, fabrication of sensors (magnetic, optical and thermal) for scanning probe microscopy, fabrication of electrical contacts and devices, and photomask repair of the next generation below the 64 nm node. For a detailed listing of applications as well as the underlying molecule dissociation mechanisms the reader is referred to a recent review [1]. Control of the process with respect to deposit thickness or etch depth is fairly well established, however, a complete physical and chemical understanding of the process is hampered by the lack of suitable means to monitor and to access the numerous interrelated and time-varying process parameters (deposition and etch rate, yield, molecule flux and adsorption/desorption).

This article will discuss in-situ monitoring of gas-assisted focused electron beam and focused ion beam deposition and etching using various signals and related setups. It will not cover in-situ observation of the process using dual or cross beam machines with both a focused electron and ion beam. Generally, such an approach will produce unwanted co-deposits from the observing beam.

2. Monitoring of stage current and secondary electron signal

These signals are collected through the substrate stage and the secondary electron (SE) detector, see fig. 2a, and are related through the current balance: I_{stage} = I_{beam} - I_{SE} - I_{BSE}. Both the number of secondary electrons (SE) and backscattered electrons (BSE) change with the sample’s topography and material. Consequently, “end-point detection” during FIB or FEB etching can be carried out by monitoring these signals: once a buried layer in the structure is reached by etching the signals will change due to the differing SE and BSE emission of materials and the process can be stopped. This technique is limited to vias holes having a high aspect ratio that still permits a significant fraction of the secondary electrons to leave the surface.

![Fig. 2a](image)

![Fig. 2b](image)

Fig. 2a: Principle of time resolved stage current monitoring. As the deposit grows, more SEs and BSEs leave the deposit through its side, augmenting the recorded SE signal and diminishing the measured stage current. The inverse holds true for particle beam induced etching. b) Example: stage current during FEB deposition of a cross-shaped deposit (Co_{25}(CO)_{8}, 25keV, 1000pA). Inset: SEM side view of the entire structure. The arrows indicate the writing direction.

Fig. 2b shows monitoring of the stage current during deposition of cross shaped deposit. The deposition starts on a lithographically pre-defined gold electrode, then the FEB is scanned to connect to the opposing gold electrode. As a result the “horizontal” line deposit is obtained. The deposition process is repeated for the “vertical” line and finally a Hall cross is obtained. Monitoring the stage current during the deposition probes the location of the electrodes (low stage current -750 pA), the substrate SiO_{2} (100 nm)/Si (high stage current -850 pA) and the first line deposit (small peak at 190 s). Together with the microscope observation and electrical measurements such a stage current plot is a fingerprint for a specific deposit geometry and deposit material. If similarly programmed deposition routines have inconsistent stage current profiles, this may indicate irregularities in the beam conditions.
(focus, beam current oscillations, drifts) or molecule supply (precursor exhaust or bursts). These signals show their full control virtue during FEB or FIB deposition of more complicated 3D structures, like pillars [2], periodic wires [3], and nanoscale artwork [4]. Of note, the stage current control was used to fabricate hole diameters in membranes smaller than the focused electron beam [5].

3. Mass sensing
When attempting to monitor the mass during FEB or FIB deposition / etching one should keep in mind that the nanodeposits feature very small masses, typically in the picogram range or below. This range can be addressed by cantilever based sensors [6]. Special care must be taken to stabilize the temperature of the setup in the milliKelvin range. The principle is given in fig. 3a and consists of a cantilever with piezoresistive readout being actuated by a piezoelectric actuator. The frequency response to mass changes must be calibrated due to the unknown cantilever force constant. This can be best achieved by monitoring the mass change while FIB milling a box of easily observable dimensions into the cantilever material. Once this calibration step is performed the mass measurements inside the microscope chamber are quantitative. From a typical dot series deposition shown in fig. 3b it can be seen that the deposition process is highly reproducible and that with increasing pillar height, the deposited mass assumes a linear dependence with time, i.e. the contributing electron fluxes (see bottom inset of fig. 3) become constant.

Fig. 3: a) Schematic diagram of the SEM integrated cantilever mass sensor for FIB/FEB induced process monitoring with local precursor supply from a microtube gas injection system. The mass added to or removed from the cantilever is detected as a negative or positive resonance frequency shift, respectively. b) FEB deposits (5kV, 300pA, dot exposure, Cu(hfa)2). Top inset: SEM tilt images of pillars deposited for 1-5 minutes. Bottom inset: contributions to mass deposition.

Furthermore, from molecule adsorption / desorption measurements (without irradiation) the monolayer coverage and the residence time of molecules on the cantilever surface can be determined. Also, deposition or etch yields, in units of deposited or etched atoms per incident electron or ion, are precisely accessible according to eqn.1:

\[ Y = \frac{N_A \cdot m / M}{I_p \cdot t / e_0} \]  

(1)

where \( I_p \cdot t \) is the incident dose during exposure time \( t \) and beam current \( I_p \), \( m \) is the measured deposited or etched mass, and \( M \) is the molar mass of the etched or deposited material. \( N_A \) is the Avogadro constant and \( e_0 \) the elementary charge. The molar mass of the etched material is generally
known and etch yields can be derived in-situ. In contrast, for deposits the composition is generally unknown and the molar mass must be determined from composition measurements. Eqn. 1 represents a means to precisely determine yields since it does not require any assumption about the deposit density. The correct deposit density \( \rho_{\text{dep}} \) of the deposit can be obtained by measuring the deposit volume \( V_{\text{dep}} \) and \( \rho_{\text{dep}} = \frac{m_{\text{dep}}}{V_{\text{dep}}} \). For the Me\(_3\)PtCpMe molecule (Me – methyl) was found [6]: 7 % monolayer coverage, a residence time of 30 \( \mu \)s, a deposit density of 11.2 g/cm\(^3\) (irradiation with 30 keV Ga\(^+\)-ions) and 4.5 g/cm\(^3\) (irradiation with 5 keV electrons). Only for precursors containing no hydrogen the density can be estimated directly from the deposit composition [7].

4. In-situ electrical resistance measurements

Time-resolved resistance measurements during gas assisted FEB deposition can be performed using pre-deposited electrodes on an insulating substrate. They will be “connected” by scanning the electron or ion beam back and forth between them which will deposit a wire, the resistance of which depends on the deposited material (electron impact molecule dissociation) and the deposited thickness. In-situ resistance measurements during FEB/FIB deposition were reported for the molecules W(CO)\(_6\) [8], Me\(_3\)PtCpMe [9, 10] and acrylic acid [1]. In-situ measurements of FIB deposited wires from Me\(_3\)PtCpMe show the formation of a Ga-phase [11] due to Joule heating, while FEB deposited freestanding wires show electromigration of platinum [12]. An example of a two point electrical resistance real-time measurement while FEB depositing with the molecule Co\(_2\)(CO)\(_8\) is shown in fig. 4.

![Fig. 4: a) FEBID of Co\(_2\)(CO)\(_8\) is performed on pre-structured Au electrodes. Electrodes active for in-situ current measurement are marked with red arrows. b) In-situ measurement of resistance evolution during deposition. Inset: evolution of deposit resistance during venting with N\(_2\).](image)

The in-situ measurements permit to study the “electrical thickness” of the deposit. For constant length, width, and homogeneous material the resistance is inversely proportional to the deposited wire thickness. Hence, for a constant deposition rate an inverse relationship between the resistance and the deposition time is obtained. Deviations from this trend point to changes affecting the charge carrier generation and kinetics, for example, by the formation of intermediate species. Also post-irradiation and air exposure phenomena can be studied and related to eventual oxidation processes, see fig. 4b. Two point measurements can be uniquely attributed to the deposit only if the contact resistance between electrodes and deposit is low compared to the deposit resistance. Alternatively, four point probe measurements would cancel contact resistance effects.

5. Reflectometry

Real-time in situ reflectometry during FEB deposition requires that a laser beam is allowed to enter into the microscope chamber. The monochromatic laser is then focused on the growing transparent or
semi-transparent deposit inside the SEM chamber and the reflected optical signal is collected by a photodiode. The principle is such that the intensity of the reflected laser beam depends on the optical thickness of the deposit and its optical absorption. A periodic signal with deposition time (deposit thickness) is obtained due to constructive and destructive interference. This allows calculating the real and imaginary parts of the diffractive index at the laser wavelength from the period and the amplitude decay after having performed a thickness calibration.

Comparing the optical thickness to the thickness measured by profilometry at various exposure times reveals if the deposited material is homogeneous or if changes in composition, i.e. the refractive index, occurred during growth. Measurements at 514 nm laser wavelength gave the following refractive indices: 1.51+i0.055 (HCOOH), 1.56+i0.14 (Si(OCH₃)₄), and 2.19+i0.013 (Ti(NO₃)₄) [13]. The value of the imaginary part is a measure for absorption and indicates that considerable amounts of carbon were co-deposited during SiO₂ deposition from the molecule Si(OCH₃)₄. The smallest absorption is evidently obtained from the carbon-free molecule (Ti(NO₃)₄). In order to perform such optical measurements the size of the deposit must be at least somewhat larger than the focused laser beam.

6. In-situ annular dark field signal
Recently, in-situ monitoring of the annular dark field (ADF) signal during electron beam induced deposition on electron transparent membranes was used to control the deposit’s thickness homogeneity [14]. This signal has a strong atomic number contrast and is assumed to depend linearly on the deposited mass. Using the signal as a feed back in the deposition process proves useful for avoiding enhanced deposition on (pre-deposited) structures having a tilt to the incident electron beam (FEBID proximity effect). With regard to the small noise on the ADF signal it was suggested that this method is capable of resolving the deposition of one single molecule. This would be the highest resolution of all the in-situ techniques employed today.

7. SEM integrated mechanical measurements
These measurements involve integration of nanomanipulation setups, comprising x, y, z stages and corresponding electronics, into the microscope chamber. A detailed overview on such cantilever based force sensors and piezo-driven vibration stages and their applications in scanning electron / ion microscopes can be found in [15]. The determination of Young’s modulus follows straightforwardly from the force balance of a reference cantilever which is gently pushed against the nanopillar under consideration, see fig. 6a. When Young’s modulus of the nanopillar is known, its density can be determined from vibration experiments as shown in fig. 6b. Mechanical properties of pillar deposits from phenanthrene, W(CO)₆, and Cu(hfa)₂ were measured from different groups and summarized in [16]. The typical range of Young’s modulus is in the order of magnitude of 10 GPa for FEB deposition.
and up to a few 100 GPa for FIB deposition [17]. Dependencies on electron or ion dose and energy were found.

![Fig. 6](image)

**Fig. 6:** a) Principle of deflection experiment. Cantilever and nanopillar are deflected according to their force constants \( k \) when moved against each other. The SEM images are taken from a video sequence and show tracking of the cantilever and substrate displacements. b) Principle of vibration experiment. When the resonance frequency of the pillar is approached the secondary electron detector measures the peak curve since the pillar vibration intersects the focused electron beam. Taken from [16].

Using a tensile stage setup, tensile strengths in the order of 1 GPa were found for FEB deposits from Co\(_2\)(CO)\(_8\) and W(CO)\(_6\) [18].

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